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SOME NEW COMPUTATIONAL AND EXPERIMENTAL TECHNIQUES FOR THE CALORIMETRIC STUDY OF SOLIDS

A THESIS

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by

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SOME NEW COMPUTATIONAL AND EXPERIMENTAL TECHNIQUES

FOR THE CALORIMETRIC STUDY OF SOLIDS

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SUMMARY

The studies which are reported in this thesis were initiated in support of a plan to provide a capability in calorimetry within the School of Chemistry. Involved in this capability were the design and construction of suitable equipment, the development of new mathematical techniques for data manipulation, and the application of these to a study of the higher-order transitions in the alkali and alkaline earth nitrites and nitrates.

The capability requirement also included the development of a mathematical expression for thermodynamic functions which accounts for most or all of the contributing effects. The use of the Born approximation was suggested for vibrational effects. Because this work was in progress before the calorimeter was completed, data from the literature were used. It was found that much greater precision than was then possible is required to justify the inclusion of terms in an expression to account for all major contributing effects.

By the use of an electronic digital computer, the Born approximation was fitted with a precision much greater than that of any previously reported work.

The work with the Born approximation suggested a new direction of study not included in the initial proposal. A new expression for calorimetric data was adopted which fits the data well and from which an approximate but realistic expression for the vibrational frequency distribu-

tion function can be extracted. Its use was demonstrated by determining the frequencies of three peaks in the vibrational spectrum of sodium chloride from calorimetric data.

It was felt that careful design could produce a calorimeter equal to or superior to existing models in precision without the use of sophisticated (and expensive) electronic controls. To satisfy this requirement, a dropping calorimeter with an isothermal receiver, employing diphenyl ether as the working medium, was selected. Its novel features are:

1. rapid approach to thermal equilibrium, both in the "furnace" and the receiver;

2. low heat exchange between the receiver and the environment, accompanied by isothermal barriers and thermal damping;

3. satisfactory operation with samples at initial temperatures both above and below ambient, overlapping the normal operating ranges of the adiabatic and dropping calorimeters;

4. an almost strainless mantle which can be quickly formed;

5. equal drift rates before and after a drop;

6. large thermal capacity (about 13000 calories) with good precision (Estimated standard error is less than 0.1 calorie over a range of -1500 to 2700 calories.);

7. two modes of "furnace" temperature control: by means of first-order transitions and controlled heat leakage; and

8. a diphenyl ether working medium with an impurity concentration of less than 0.1 percent.

The calorimeter was used to measure the enthalpy of sodium nitrite from 195°K to 450°K with special emphasis on the temperature region near

437°K. Two higher-order transitions were found: one at 436.65°K and one at 437.65°K. The smaller of these showed an enthalpy of transition of only five calories/mole.

CHAPTER I

INTRODUCTION

The determination of the thermodynamic properties of solids is the oldest technique in the field of calorimetry. The technique has been developed in recent years into one of the most precise physical methods which can be performed. In spite of the great precision, the use of calorimetric measurements has some severe limitations. First, a calorimeter for solids can measure directly only one thermodynamic function, enthalpy change as a function of temperature and volume. Absolute enthalpy values must be estimated by extrapolation to the absolute zero of the temperature scale. Some thermodynamic functions other than enthalpy can be derived by suitable manipulation of the calorimetric data alone, but some of the more interesting ones require additional information. The second limitation is the tantalizing one. The enthalpy function contains a wealth of information about the physical behavior of a solid. Included in the enthalpy function are the vibrational frequency distribution function, phase changes, order-disorder phenomena, rotational effects, electronic effects, and others. These effects are not easily studied quantitatively using calorimetric measurements, however, because only the resultant of all of the effects is available.

Numerical techniques for interpolation, extrapolation, integration and differentiation of calorimetric data to extend their usefulness are well established. One of the more useful tools for these operations is

the fitted mathematical expression. The use of the polynomial fitted by least-squares methods for interpolation, integration, and differentiation has become almost universal. In fact, the polynomial is frequently used alone in reports of calorimetric studies rather than the data which it represents because of its conciseness. Extrapolation cannot be satisfactorily accomplished without some recourse to fundamental principles, but much success has been gained in this area by the use of the Born approximation, notably in the calculation of absolute entropies. It is now possible to measure enthalpy changes in solids with a precision that is not preserved in the fitted expressions. One object of this study is the application of improved fitting expressions and techniques. More than usual detail of the background is given because complete sets of calorimetric expressions are not readily available in the literature.

By the methods of solid-state physics, it is now possible to compute, from first principles, the vibrational frequency distribution function of some simple crystals. The derivation of this distribution function from calorimetric data, however, has been an elusive goal. One approach, frequently used in the past, is the adoption of a particular expression for the distribution function. This expression has been selected either to conform to a simplified model or for computational convenience, and bears no resemblance to distribution functions derived from first principles or from observed vibrational spectra. Using some of the constraints imposed by solid-state physics and an expression which can represent any vibrational frequency distribution function reasonably well, it is possible to derive an approximate distribution of frequencies from calorimetric data. Such a derivation developed as a by-product of work

on mathematical expressions for calorimetric data.

A further object of this study was the design and construction of an inexpensive calorimeter system which could compete favorably with the best of those found in other laboratories. There is, of course, no calorimeter design which performs well in all temperature ranges. The ranges of the two most frequently used designs overlap somewhat in the vicinity of ordinary room temperature, and the data from the two do not agree well in the overlap region. It was felt that the new design should complement other models in this region and provide useful data well below and well above it. To demonstrate the system, a study of sodium nitrite was proposed.

Because all phases of this study ran concurrently, it was not possible to follow a logical scheme of calorimeter design followed step-by-step by other phases leading eventually to interpretation of the results. In addition, the derivation of a vibrational frequency distribution function for a crystal as complex as sodium nitrite must wait for the advent of faster electronic computers or the dedication of an existing computer to the problem for a very long time. For these reasons, work on mathematical expressions was performed with data from the literature. The calorimeter was designed, built, and tested independently.

CHAPTER II

THE USE OF MATHEMATICAL EXPRESSIONS TO INTERPRET CALORIMETRIC DATA

Existing calorimeters designed for the study of solids are capable of measuring only one thermodynamic function; that function is the variation of enthalpy with temperature and volume under conditions of constant, usually atmospheric, pressure.* The enthalpy function, however, holds most of the information needed to derive all of the other thermodynamic functions and, if the measurements of it were sufficiently precise, to determine the vibrational frequency distribution function. The equation of state, or at least the variation of the compressibility and coefficient of expansion with temperature, is needed to compute the internal energy, Helmholtz free energy, and heat capacity at constant volume. Any attempt to approximate the vibrational frequency distribution function requires, in addition to the equation of state, a means of isolating the vibrational contribution to the enthalpy function.

The Expressions

A convenient tool for manipulating thermodynamic functions for thermochemical calculations is a mathematical expression which has been

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*In this work, the function is referred to as $H(T,v)$ when it is desirable to emphasize the constant-pressure restriction. Otherwise, it is referred to conventionally as $H_T - H_{\text{reference temperature}}$. A superscript zero is used to identify a reference to a standard state.

fitted to an enthalpy function or to some derived function, such as heat capacity at constant pressure, which has been computed from the enthalpy function by other means. Such an expression may be entirely empirical and still be very useful. It is interesting and potentially very useful to attempt to derive expressions based as closely as possible on a reasonable model of the solid. Such an expression must take into account vibrational effects, non-vibrational effects, such as transitions, and the equation of state.

Vibrational Effects

There has been much research directed toward understanding vibrational effects in crystalline solids. Such work is based primarily on statistical mechanical considerations. It is convenient in such work to ignore the effect of lattice expansion or contraction; therefore, enthalpy, heat capacity at constant pressure, and Gibbs' free energy are not studied directly. Expressions for internal energy, heat capacity at constant volume, Helmholtz' free energy, and entropy can be derived from these by the use of the equation of state.

On the following pages, for reference purposes, some of the important mathematical expressions for thermodynamic functions and their derivation are given.

The Einstein Functions

The assumption that internal energy is a linear function of temperature is supported by classical mechanics. To be precise

$$U = 3RT$$

The first to invoke the quantum theory in the study of the thermodynamics of crystals was Einstein. Einstein accepted the quantization of energy suggested by Planck and applied the principle to the vibrational energy of atoms within a crystal lattice.

The expression for the internal energy in terms of the partition function, f, is

$$U_T - U_0^\circ = NkT^2 \left(\frac{\partial \ln f}{\partial T}\right)_v$$

Assuming that all of the atoms of the lattice vibrate with the same frequency, by Planck's hypothesis

$$\epsilon = (i + \tfrac{1}{2})h\nu \qquad i = 0, 1, 2, \ldots$$

If the degeneracy of each oscillator is ω, the partition function is

$$f = \left[\omega \sum_{i=1}^{\infty} e^{-(i+\frac{1}{2})h\nu/kT}\right]^3 = \frac{\omega^3 \, e^{-\frac{3}{2}h\nu/kT}}{\left(1 - e^{-h\nu/kT}\right)^3}$$

$$\ln f = 3\ln \omega - \tfrac{3}{2}h\nu/kT - 3\ln\left(1 - e^{-h\nu/kT}\right)$$

$$\left(\frac{\partial \ln f}{\partial T}\right)_v = 0 + \tfrac{3}{2}h\nu/kT^2 + \frac{3\frac{h\nu}{kT^2}\, e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

$$= \frac{3h\nu}{kT^2}\left[\tfrac{1}{2} + \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}\right] = \frac{3h\nu}{kT^2}\left[\tfrac{1}{2} + \frac{1}{e^{h\nu/kT} - 1}\right]$$

$$U_T - U_o^o = 3Nh\nu \left[\frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1}\right]$$

$$C_v = \frac{3N\ (h^2\nu^2/kT^2\ e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$F_T - U_o^o = \frac{3}{2}Nh\nu - 3NkT \ln\ (\omega/(1 - e^{-h\nu/kT}))$$

$$S = 3Nk\left[\frac{h\nu/kT}{e^{h\nu/kT} - 1} + \ln\ (\omega/(1 - e^{-h\nu/kT}))\right]$$

Assuming that the states are not degenerate

$$F_T - U_o^o = \frac{3}{2}Nh\nu + 3NkT \ln\ (1 - e^{-h\nu/kT})$$

$$S = 3Nk\left[\frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln\ (1 - e^{-h\nu/kT})\right]$$

In the assumed model, ν represents the common frequency of all atoms in the crystal lattice. For a real material, ν may be considered to be a characteristic constant which may be determined by fitting the internal energy expression to a set of experimental values. The experimental values are never absolute; for this reason a second constant, the absolute internal energy at the reference temperature, must also be determined.

The Nernst-Lindemann Functions

The Einstein expressions are useful for interpolation at reason-

ably high temperatures but fail at low temperatures and are useless for extrapolation to the absolute zero. The problem, of course, is that solids have complex frequency distribution functions and the assumption that all atoms vibrate at the same frequency is a poor one. Much improvement was obtained by Nernst and Lindemann, who assumed that there are two fundamental vibrational frequencies, but even the improved formula was not useful for extrapolation.

A General Partition Function for Vibrational Energy in Solids

For an orderly development of interpolating and extrapolating expressions, what is needed is an expression for the partition function in terms of the vibrational frequency distribution function.

For each normal coordinate, a partition function, f_i, may be defined

$$f_i = \omega \sum_{j=o}^{\infty} e^{-(j+\frac{1}{2})h\nu_i/kT} = \frac{\omega\, e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/kT}}$$

The partition function for the whole system is

$$f^N = \prod_{i=1}^{3N} f_i = \omega^{3N} \prod_{i=1}^{3N} \frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu/kT}}$$

$$\ln f = 3\ln \omega - \frac{h}{2kT} \sum_{i=1}^{3N} \nu_i - \sum_{i=1}^{3N} \ln (1 - e^{-h\nu_i/kT})$$

Let the vibrational distribution function be $g(\nu)$. $g(\nu)$ must satisfy

the normalization condition

$$\int_0^\infty g(\nu)\, d\nu = 3N$$

Therefore, in any real problem, $g(\nu)$ must approach zero in the finite frequency range.

$$\sum_{i=1}^{3N} \nu_i = \int_0^\infty \nu g(\nu)\, d\nu$$

$$\sum_{i=1}^{3N} \ln\left(1 - e^{-h\nu_i/kT}\right) = \int_0^\infty \ln\left(1 - e^{-h\nu/kT}\right) g(\nu)\, d\nu$$

$$\ln f = 3\ln \omega - \frac{h}{2kT}\int_0^\infty \nu g(\nu)\, d\nu - \int_0^\infty \ln\left(1 - e^{-h\nu/kT}\right) g(\nu)\, d\nu$$

$$U_T - U_o^o = \frac{h}{2}\int_0^\infty \nu g(\nu)\, d\nu + h\int_0^\infty \frac{\nu g(\nu)\, d\nu}{e^{h\nu/kT} - 1}$$

$$C_v = \int_0^\infty \frac{(h^2\nu^2/kT^2)\, e^{h\nu/kT}\, g(\nu)\, d\nu}{(e^{h\nu/kT} - 1)^2}$$

$$F_T - U_o^o = \frac{h}{2}\int_0^\infty \nu g(\nu)\, d\nu + kT\int_0^\infty g(\nu)\ln\left(1 - e^{-h\nu/kT}\right) d\nu - 3NkT\ln\omega$$

$$S = \frac{h}{T}\int_0^\infty \frac{\nu g(\nu)\, d\nu}{e^{h\nu/kT} - 1} - k\int_0^\infty g(\nu)\ln\left(1 - e^{-h\nu/kT}\right) d\nu + 3Nk\ln\omega$$

The Debye Functions

Debye took as his model for a crystalline solid a material composed of atoms, for the sake of defining

$$\int_0^\infty g(\nu)\, d\nu$$

but which behaved mechanically as an elastic continuum. The vibrational frequency distribution for a continuum is

$$g(\nu) = 4\pi V \left(\frac{1}{c_\ell^3} + \frac{2}{c_t^3}\right) \nu^2$$

where V is the volume and c_ℓ and c_t are the speeds of propagation in the longitudinal and transverse directions. Because $g(\nu)$ is a monotonically increasing function, normalization is accomplished by imposing an arbitrary cut-off frequency, ν_m. V, c_ℓ, and c_t may be eliminated by normalization

$$4\pi V \left(\frac{1}{c_\ell^3} + \frac{2}{c_t^3}\right) \int_0^{\nu_m} \nu^2\, d\nu = 3N$$

$$\frac{4\pi V\, \nu_m^3}{3} \left(\frac{1}{c_\ell^3} + \frac{2}{c_t^3}\right) = 3N$$

$$4\pi V \left(\frac{1}{c_\ell^3} + \frac{2}{c_t^3}\right) + \frac{9N}{\nu_m^3}$$

This operation makes ν_m a quantity which is characteristic of the material; it may not be taken to be infinite.

$$g(\nu) = \frac{9N}{\nu_m^3}\,\nu^2$$

$$U_T - U_o^o = \frac{h}{2}\int_o^{\nu_m} \frac{9N}{\nu_m^3}\,\nu^3\,d\nu + h\int_o^{\nu_m} \frac{\frac{9N}{\nu_m^3}\,\nu^3\,d\nu}{e^{h\nu/kT} - 1}$$

$$= \frac{9Nh\,\nu_m}{8} + \frac{9Nh}{\nu_m^3}\int_o^{\nu_m} \frac{\nu^3\,d\nu}{e^{h\nu/kT} - 1}$$

This expression may be changed to the more familiar form by change of variable.

Let $y = \frac{h\nu}{kT}$ and $x = h\nu_m/kT$.

Then $\nu = kTy/h$ and $d\nu = kTdy/h$.

$$U_T - U_o^o = 9NkT\left[\frac{x}{8} + \frac{1}{x^3}\int_o^x \frac{y^3dy}{e^y - 1}\right]$$

$$C_v = 9Nk\left[\frac{4}{x^3}\int_o^x \frac{y^3dy}{e^y - 1} - \frac{x}{e^x - 1}\right]$$

$$F_T - U_o^o = 9NkT\left[\frac{x}{8} + \frac{1}{x^3}\int_o^x y^2 \ln\left(1 - e^{-y}\right) dy\right] - 3NkT \ln \omega$$

$$S = \frac{9Nk}{x^3}\left[\int_o^x \frac{y^3dy}{e^y - 1} - \int_o^x y^2 \ln\left(1 - e^{-y}\right) dy\right] + 3Nk \ln \omega$$

The expressions for $F_T - U_o^o$ and S may be simplified somewhat by integration by parts.

$$F_T - U_o^o = 3NkT \left[\frac{3x}{8} - \frac{1}{x^3}\int_o^x \frac{y^3 dy}{e^y - 1} + \ln (1 - e^{-x})\right] - 3NkT \ln \omega$$

$$S = 3Nk \left[\frac{4}{x^3}\int_o^x \frac{y^3 dy}{e^y - 1} - \ln (1 - e^{-x})\right] + 3Nk \ln \omega$$

These expressions are not in agreement with those of Giguère and Boisvert.[1]

The Born-von Kármán Functions

Concurrently with Debye's studies, Born began his studies of lattice dynamics. Born and von Kármán worked out an approximate spectrum for a three-dimensional lattice by analogy with the case of the linear chain. The mathematical development is given in detail in references 2, 3, and 4. The distribution function is

$$g(\nu) = \frac{9N^3 [\sin^{-1} (\nu/\nu_o]^2}{\pi^3 (\nu_o^2 - \nu^2)^{\frac{1}{2}}}$$

where ν_o is a characteristic constant. At high temperatures the Born and von Kármán functions behave very much as the Debye functions. They are less successful for extrapolation to low temperatures than the Debye functions.

The Barber and Martin Function

In 1959, Barber and Martin[5] published a report of their development of "A Heat Capacity Function with Velocity Dispersion for Isotropic

Solids." It is said to be particularly useful for monatomic solids. They fitted one such expression to the heat capacity function of aluminum with good results. Their expression has the form

$$\frac{C_v}{3R} = \frac{24}{\pi^3 x_o} \int_o^{\theta/T} \frac{x^2 \, e^x \, [\sin^{-1} (x/x_o)]^2 \, dx}{(e^x - 1)^2 \sqrt{1 - (x/x_o)^2}}$$

where $x = h\nu/kT$ and $x_o = \theta/T$ where θ is a characteristic constant equal to $2\theta_D/\pi$.

All of the expressions listed up to this point apply in a strict sense only to monatomic solids. Those which follow apply to all crystalline solids. The normalization condition is

$$\int_o^{\infty} g(\nu) \, d\nu = 3Ns$$

where s is the number of particles in the unit cell.

The Born Approximation

The Born lattice theory[6] and subsequent work in lattice dynamics by Blackman[4] and others[7,8] are enticing because they provide the framework for calculation of the frequency distribution functions of crystalline solids from first principles. The derivation is given in detail in the references cited.

The result of the lattice theory may be expressed as a secular equation of order 3s (a set of 3s homogeneous linear equations). The sum of the 3s solutions represents the frequency distribution function. Three of these solutions represent broad distribution branches concen-

trated at low frequencies. The other 3s-3 solutions represent usually narrow branches which may be found in any frequency region. There is no closed form solution in any real case. Some simple cases have been solved by the use of high-speed computing equipment. Born, however, found the solution too laborious to be attempted and suggested an approximate solution

$$g(\nu) = \sum_{i=1}^{3} \delta_i(\nu) + \sum_{i=4}^{3s} \epsilon_i(\nu)$$

where δ, the Debye distribution, represents an acoustic solution and ϵ, the Einstein distribution, represents an optical solution. This distribution function leads to the expressions

$$U_T - U_o^o = \sum_{i=1}^{3} \frac{3NkT}{\left(\frac{\theta_i}{T}\right)^3} \int_o^{\theta_i/T} \frac{y^3 dy}{e^y - 1} + \sum_{i=4}^{3s} \frac{Nh\nu_i}{e^{h\nu_i/kT} - 1}$$

$$C_v = \sum_{i=1}^{3} 3Nk \left[\frac{4}{(\theta_i/T)} \int_o^{\theta_i/T} \frac{y^3 dy}{e^y - 1} - \frac{\theta_i/T}{e^{\theta_i/T} - 1}\right]$$

$$+ \sum_{i=4}^{3s} \frac{N \left(\frac{h^2 \nu_i^2}{kT^2}\right) e^{h\nu_i/kT}}{\left(e^{h\nu_i/kT} - 1\right)^2}$$

$$F_T - U_o^o = \sum_{i=1}^{3} NkT \left[\ln\left(1 - e^{-\theta_i/T}\right) - \left(\frac{T}{\theta_i}\right)^3 \int_o^{\theta_i/T} \frac{y^3 dy}{e^y - 1}\right]$$

$$+ \sum_{i=4}^{3s} NkT \ln \left(1 - e^{-h\nu_i/kT}\right)$$

$$S = \sum_{i=1}^{3} Nk \left[4 \left(\frac{T}{\theta_i}\right)^3 \int_0^{\theta_i/T} \frac{y^3 dy}{e^y - 1} - \ln \left(1 - e^{-\theta_i/T}\right)\right]$$

$$+ \sum_{i=4}^{3s} Nk \left[\frac{h\nu_i/kT}{e^{h\nu_i/kT} - 1} - \ln \left(1 - e^{-h\nu_i/kT}\right)\right]$$

where $\theta_i = h(\nu_m)_i/k$.

A New Set of Mathematical Expressions for Thermodynamic Properties of Solids

Frequency distribution functions derived from observed spectra or from lattice theory show little similarity to any of those discussed so far. Lattice theory shows that there are 3s branches of the distribution function, where s is the number of atoms in the unit cell. Three of these branches begin at the origin, go through a maximum, and return to zero at frequencies determined by the dimensions of the first Brillouin zone of the crystal. The other 3s-3 branches display maxima and limiting frequencies but are displaced from the origin. The resultant of all the branches is a continuous curve (though its first derivative may be discontinuous), which usually exhibits several maxima and has a zero value above some limiting frequency. Such a function can be expressed with a good degree of approximation by a sum of Gaussian terms

$$g(\nu) = \sum_{i=1}^{3s} a_i \, e^{-b_i(\nu - c_i)^2}$$

where the a_i are characteristic amplitudes, the b_i determine the band width, and the c_i are characteristic frequencies. The quantities a_i, b_i, and c_i are not independent. The b_i may be eliminated by normalization

$$\int_0^\infty g(\nu)\, d\nu = 3Ns$$

$$\int_0^\infty a_i \, e^{-b_i(\nu - c_i)^2} \, d\nu = N$$

a_i, b_i, and c_i can be chosen so that

$$\int_0^\infty a_i \, e^{-b_i(\nu - c_i)^2} \, d\nu \simeq \int_{-\infty}^\infty a_i \, e^{-b_i(\nu - c_i)^2} \, d\nu = N = \frac{a_i \sqrt{\pi}}{\sqrt{b_i}}$$

$$b_i = \frac{\pi a_i^2}{N^2}$$

$$g(\nu) = \sum_{i=1}^{3s} a_i \, e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2}$$

This distribution function leads to the expressions

$$U_T - U_o^o = \int_0^\infty \left[\frac{h\nu}{e^{h\nu/kT} - 1}\right] \cdot \left[\sum_{i=1}^{3s} a_i \, e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2}\right] d\nu$$

$$C_v = \int_o^\infty \left[\frac{(h^2\nu^2/kT^2)\ e^{h\nu/kT}}{(e^{h^2/kT} - 1)^2} \right] \cdot \left[\sum_{i=1}^{3s} a_i\ e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2} \right] d\nu$$

$$S = k \int_o^\infty \left[\frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln\left(1 - e^{-h\nu/kT}\right) \right] \cdot \left[\sum_{i=1}^{3s} e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2} \right] d\nu$$

$$F_T - U_o^o = kT \int_o^\infty \left[\ln\left(1 - e^{-h\nu/kT}\right) \right] \cdot \left[\sum_{i=1}^{3s} e^{\frac{\pi a_i^2}{N^2}(\nu - c_i)^2} \right] d\nu$$

The approximation used above is valid only if the area under the frequency distribution curve at frequencies less than zero is negligible. The values of a_i and c_i for which this condition are met are given by

$$\lim_{\nu \to 0} T(\nu) \ll \lim_{\nu \to c_i} T(\nu)$$

where $T(\nu)$ is the integrand in the expression for one of the thermodynamic functions. For the heat capacity at constant volume, this relation is

$$\lim_{\nu \to 0} \frac{(h^2\nu^2/kT^2)(e^{h\nu/kT})(a\ e^{-\frac{\pi a^2}{N^2}(\nu - c)})}{(e^{h\nu/kT} - 1)^2} \ll \lim_{\nu \to c} \frac{(h^2\nu^2/kT^2)(e^{h\nu/kT})(a\ e^{-\frac{\pi a^2}{N^2}(\nu - c)})}{(e^{h\nu/kT} - 1)^2}$$

The right-hand side of the inequality is given by

$$\frac{a\,(h^2c^2/kT^2)\,e^{hc/kT}}{(e^{hc/kT}-1)^2}$$

The left-hand side may be evaluated by repeated application of l'Hospitals' rule. Let LIM represent the left-hand side. Applying l'Hospitals' rule once

$$LIM = \lim_{\nu \to 0} \frac{\frac{d}{d\nu}\left[\left(\frac{h^2\nu^2}{kT^2}\right)\left(e^{h\nu/kT}\right)\left(a\,e^{-\frac{\pi a^2}{N^2}(\nu-c)^2}\right)\right]}{\frac{d}{d\nu}\left[\left(e^{h\nu/kT}-1\right)^2\right]}$$

$$= \lim_{\nu \to 0} \left\{\left[\left(\frac{h^2\nu^2}{kT^2}\right)\left(e^{h\nu/kT}\right)\left(-\frac{2\pi a^3}{N^2}\right)(\nu-c)\left(e^{\frac{\pi a^2}{N^2}(\nu-c)^2}\right)\right.\right.$$

$$+\left(\frac{h^2\nu^2}{kT^2}\right)\left(\frac{h\,e^{h\nu/kT}}{kT}\right)\left(e^{-\frac{\pi a^2}{N^2}(\nu-c)^2}\right)$$

$$\left.+\left(\frac{2h^2\nu}{kT^2}\right)\left(e^{h\nu/kT}\right)\left(a\,e^{-\frac{\pi a^2}{N^2}(\nu-c)^2}\right)\right]\Big/$$

$$\left.\left[2\left(e^{h\nu/kT}-1\right)\left(\frac{h\,e^{h\nu/kT}}{kT}\right)\right]\right\}$$

LIM is still indeterminate. Applying l'Hospitals' rule again

$$\lim_{\nu \to 0}\frac{d}{d\nu}(\text{denominator}) = \lim_{\nu \to 0}\left[2\left(e^{h\nu/kT}-1\right)\left(\frac{h^2\,e^{h\nu/kT}}{k^2T^2}\right)+\left(\frac{h\,e^{h\nu/kT}}{kT}\right)^2\right]$$

$$= \frac{2h^2}{k^2T^2}$$

which is finite and non-zero. There is only one non-zero term in

$$\lim_{\nu \to 0} \frac{d}{d\nu} \text{ (numerator)}$$

namely, the addend in the derivative of the third term which contains the derivative of its first factor

$$\lim_{\nu \to 0} \frac{d}{d\nu} \text{ (numerator)} = \lim_{\nu \to 0} \left[\left(\frac{2h^2 \, e^{h\nu/kT}}{kT^2}\right)\left(a \, e^{-\frac{\pi a^2}{N^2}(\nu - c)^2}\right)\right]$$

$$= \left(\frac{2h^2}{kT^2}\right)\left(a \, e^{-\frac{\pi a^2 c^2}{N^2}}\right)$$

$$\text{LIM} = \frac{2h^2 a \, e^{\frac{\pi a^2 c^2}{N^2}}}{\frac{2h^2}{k^2T^2}} + ak \, e^{-\frac{\pi a^2 c^2}{N^2}}$$

It is necessary, then, that all a_i and c_i be chosen so that

$$k \, e^{-\frac{\pi a_i^2 c_i^2}{N^2}} \ll \frac{(h^2c^2/kT^2) \, e^{hc/kT}}{(e^{hc/kT} - 1)^2}$$

for calculations of C_v. For calculations of the internal energy, $U_T - U_o^o$,

it is necessary that

$$k\, e^{-\frac{\pi a_i^2 c_i^2}{N^2}} \ll \frac{hc_i}{e^{hc_i/kT} - 1}$$

for all a_i and c_i.

Lattice Expansion

The effect of lattice expansion on heat capacity is given by the expression

$$C_p = C_v - T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p^2 = C_v + \frac{\alpha^2\, v\, T}{k}$$

where

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

is the coefficient of expansion and

$$k = -\frac{1}{v}\left(\frac{\partial p}{\partial v}\right)_T$$

is the compressibility. Both α and k are functions of temperature and pressure. Values of α and k along the one-atmosphere isobar from 0°K through the temperature region of interest must be known to calculate the internal energy, U(T,p), from H(T,v) according to the relation

$$U_T - U_o^o = H_T - U_o^o - \int_o^T \frac{\alpha^2\, v y dy}{k}$$

Several approximate expressions have been used. These are usually ex-

pressed in terms of $C_p - C_v$. The Grüneisen approximation[9] is

$$C_p - C_v = aC_p^2T$$

The Nernst approximation[10] is

$$C_p - C_v = a'T^{\frac{3}{2}}$$

It is usually used in the more general form

$$C_p - C_v = a'T^b$$

Kelley,[11] in work with the Born approximation, chooses to ignore $C_p - C_v$ and allow the effects of lattice expansion to be absorbed by the parameters of the mathematical expression. This procedure is equivalent to assuming that the energy of lattice expansion can be represented by a Born expression. The general shape of $C_p - C_v$ versus temperature curves supports this choice, as does Kelley's success in fitting the Born approximation to experimental data. It was found in this work that the addition of one Einstein term to the Born approximation is even more satisfactory.

Transitions

First-order transitions must be treated mathematically as limit points; the expressions for thermodynamic properties on each side of the transition temperature must be independent. For energy expressions, there must be an additive constant term (equal to the transition energy) above the transition temperature.

Electronic transitions are expressed exactly by the Schottky relations[12]

$$\Delta U = N\omega_2 \epsilon/(\omega_1 \ e^{\epsilon/kT} + \omega_2)$$

$$\Delta C_v = Nk \left(\frac{\epsilon}{kT}\right)^2 \frac{\omega_1 \ \omega_2 \ e^{\epsilon/kT}}{(\omega_1 \ e^{\epsilon/kT} + \omega_2)^2}$$

where ω_1 and ω_2 are the statistical weights of the two possible states and ϵ is the energy difference between them.

No adequate expression has been found for all high-order transitions. For the $(NH_4)_2SO_4$ lambda transition, limited success was obtained with the expressions

$$\Delta C_p = a \exp(-b(c - T)^d) \qquad (T < c);$$

$$\Delta C_p = a \exp(-b'(T - c)^{d'}) \qquad (T > c)$$

The function is entirely empirical.

Curve Fitting

The expressions given in previous sections can be summed as needed to produce a fairly accurate model for the thermodynamic properties of a crystalline solid. It should be possible to fit an expression formed in this way to experimental values of enthalpy or heat capacity to a degree of precision within the experimental error. If the model were perfect and the data were exact, the fitted expression could be separated to show the

contributions due to each effect involved in the thermodynamic property expressed. Because of imperfections in the model and the data, and because considerable over-specification by the data is necessary to obtain a valid fit, the parameters of the expression are not independent and some distortion of them is inevitable. This distortion is not important in most problems, which require only a precise representation of the thermodynamic properties. The precision of calorimetric measurements is not yet sufficiently great to allow the evaluation of many parameters in the fitted expression without considerable distortion. In this work, the number of parameters was kept as small as possible. It has been shown in this work, however, that meaningful information concerning the vibrational frequency distribution of a simple crystal can be obtained by isolating the vibrational effects.

Calculation of the various thermodynamic properties of crystalline solids from calorimetric data requires the differentiation and integration of enthalpy or heat capacity functions. Over wide temperature intervals, these operations have been customarily performed by graphical or numerical methods with a reasonably high degree of precision. In cases where a narrower temperature interval or a lower degree of precision could be tolerated, most workers have found it more convenient to fit to the data integrable and differentiable expressions on which the necessary mathematical operations could be easily performed. The most frequently encountered expression, almost to the exclusion of all others, is the polynomial in temperature. Polynomials can, in principle, represent the data to any desired degree of precision. In addition, polynomials are easily integrated and differentiated. Techniques for fitting polynomials

are well developed. In practice, however, it has been found that many terms are required for a fit that is within the experimental error of the observations. Because of the almost universal acceptance of polynomials, it was deemed desirable to provide means for polynomial fitting. Digital computer algorithms to do this were written and tested and added to the program library.

Alternatives to polynomials for the interpretation and manipulation of calorimetric data have not been used frequently, probably because the more reasonable alternatives cannot be treated as linear expressions. Non-linear methods of curve fitting are tedious and give no promise of ultimate success. They usually require that the user have some idea of what the result will be before he starts. Because of the complex shape of the error hypersurface, it is possible for a non-linear fitting method to fail because of entrapment in a false minimum. For these reasons, non-linear fitting methods must be used with great care and cannot be embodied in a "black-box" algorithm for indiscriminate use. There are, however, several classical methods which, with care, give good results. Two of the more widely used methods are the Newton-Raphson method and the method of steepest descents. A very promising method which has not been widely used is the "letagrop" (pit-mapping) method of Sillén.[13] The Newton-Raphson method was selected for this work.

The Newton-Raphson Method

Briefly, the Newton-Raphson method may be described as follows. The least-squares condition is that

$$\sum_{i=1}^{n} \omega_i (f_i(x_1, x_2, \ldots, x_m, z_1, z_2, \ldots, z_p) - y_i)^2 \qquad (1)$$

be a minimum. In this expression, f is a trial function to be fitted, the z are independent variables, p is the number of independent variables, the x are parameters which may be adjusted to produce the minimum, m is the number of adjustable parameters, y is the dependent variable, ω is its statistical weight, and n is the number of observations. The function represented by this expression has a minimum (or maximum) when its partial derivatives with respect to all x are zero

$$2\sum_{i=1}^{n} \omega_i (f_i(x_1, x_2, \ldots, x_m, z_1, z_2, \ldots, z_p) - y_i) \frac{\partial f_i}{\partial x_k} = 0 \qquad (2)$$

for k = 1,2,...,m. Expanded in the Taylor series, the trial function may be expressed

$$f(x_1, x_2, \ldots, x_m, z_1, z_2, \ldots, z_p) = \sum_{j=1}^{m} c_j \frac{\partial f}{\partial x_j} + f(x_1 - c_1, x_2 - c_2, \ldots, \qquad (3)$$

$$x_m - c_m, z_1, z_2, \ldots, z_p) + \ldots$$

where the c are undetermined corrections to known approximate values of the x. This expression is not rigorous if terms of order higher than the first are ignored, but it may be used to improve approximate values of the x.

Substituting f from Equation 3 into Equation 2, one obtains

$$\sum_{i=1}^{n} \omega_i \left(\sum_{j=1}^{m} c_j \frac{\partial f_i}{\partial x_k} - r_i \right) \frac{\partial f_i}{\partial x_k} = 0 \qquad (4)$$

for k = 1,2,...,m, where

$$r_i = y_i - f_i(x_1, x_2, \ldots, x_m, z_1, z_2, \ldots, z_p) \tag{5}$$

Equation 4 may be written more compactly in matrix form

$$D^T \Omega D c = D^T \Omega r \tag{6}$$

where D is an n x m matrix of the partial derivatives of the trial function with respect to each adjustable parameter evaluated at each set of values of the independent variables, Ω is an n x n diagonal matrix of the statistical weights, D^T is the transpose of D, c is an m x 1 column matrix of corrections to be evaluated, and r is an n x 1 column matrix of the residuals for each observation. The corrections, then, are given by

$$c = (D^T \Omega D)^{-1} D^T \Omega r \tag{7}$$

The Newton-Raphson method does not always converge because it neglects terms of order higher than the first in the Taylor series. Unless the initial values of the adjustable parameters are particularly bad, the corrections calculated by this method will always have the proper sign, but may be too large in absolute value to permit convergence. The absolute values of the corrections may be reduced, if necessary, by increasing the absolute values of the diagonal elements of $D^T \Omega D$.[14] This change may be made by multiplying the diagonal terms of $D^T \Omega D$ by positive numbers greater than unity. It is difficult (and sometimes impossible)

to determine, a priori, the minimum values of these multipliers, but satisfactory values may be found experimentally.

Fitting the Born Approximation

Although the Born approximation has not found widespread public acceptance, its use has been growing in recent years and it has been found almost indispensable in some applications. One such application is the extrapolation of heat capacity curves from the measurement at the lowest practical temperature to 0°K for absolute entropy calculations. Polynomials are, of course, useless for such extrapolation. A practical advantage to the use of the Born approximation is that the Debye and Einstein terms are even more easily interconverted among the thermodynamic functions because of the existence of tables for this purpose.[15, 1] The Born approximation is much more difficult to fit than a polynomial, however, and, up to now, only graphical and trial-and-error methods have been used. These result in a precision of about one to five percent. Kelley[16] suggests that an allowance for error of five to ten percent is acceptable if the Born approximation is to be used only for the extrapolation of heat-capacity data below 50°K to determine absolute entropies. To demonstrate their full usefulness, however, the expressions must be fitted much more precisely.

Present calorimetric data do not require or justify the use of all of the terms in the Born approximation. Kelley recommends the combination of terms which differ only in the direction of the vibration and that $C_p - C_v$ be absorbed by the proper selection of the parameters. The result is that only one Debye term and s-1 Einstein term(s) are used. Given these restrictions, it becomes unreasonable to fix the values of

the coefficients of the Debye and Einstein terms; thus, in this work, they are also made adjustable parameters. The resulting modified Born approximation has the form

$$C_p = a_1 D(b_1/T) + \sum_{i=2}^{s} a_i E(b_i/T) = \frac{12 a_1 T^3}{b_1^3} \int_0^{b_1/T} \frac{y^3 dy}{e^y - 1}$$

$$- \frac{3 a_1 b_1}{T(e^{b/T} - 1)} + \sum_{i=2}^{s} \frac{a_i b_i^2 e^{b_i/T}}{T^2 (e^{b_i/T} - 1)^2}$$

$$H_T - H_0^o = a\, D(b\ /T) + \sum_{i=2}^{s} a_i E(b_i/T) = \frac{3 a_1 T^4}{b_1^3} \int_0^{b_1/T} \frac{y^3 dy}{e^y - 1}$$

$$+ \sum_{i=2}^{s} \frac{a_i b_i}{e^{b_i/T} - 1}$$

In each expression, D represents the appropriate Debye expression and E represents the appropriate Einstein expression.

Digital computer algorithms were written to fit the Born approximation, with or without these restrictions, to calorimetric data, using the Newton-Raphson method described earlier. The required partial derivatives are as follows

$$\frac{\partial C_p}{\partial a_1} = D(b_1/T)$$

$$\frac{\partial C_p}{\partial b_1} = \frac{3 a_1}{b_1} \left(\frac{b_1^2 e^{b_1/T}}{T^2 (e^{b_1/T} - 1)^2} - D(b_1/T) \right)$$

$$\frac{\partial C_p}{\partial a_i} = E(b_i/T)(i > 1)$$

$$\frac{\partial C_p}{\partial b_i} = a_i \left(E(b_i/T)\right)\left(\frac{1}{T} + \frac{2}{b_i} - \frac{2e^{b_i/T}}{T(e^{b_i/T} - 1)}\right)(i > 1)$$

$$\frac{\partial (H_T - H_o^o)}{\partial a_1} = D(b_1/T)$$

$$\frac{\partial (H_T - H_o^o)}{\partial b_1} = \frac{3a_1}{b_1}\left(\frac{b_1}{e^{b_1/T} - 1} - D(b_1/T)\right)$$

$$\frac{\partial (H_T - H_o^o)}{\partial a_i} = E(b_i/T)(i > 1)$$

$$\frac{\partial (H_T - H_o^o)}{\partial b_i} = a_i \left(\frac{1}{e^{b_i/T} - 1} - \frac{b_i e^{b_i/T}}{T(e^{b_i/T} - 1)^2}\right)(i > 1)$$

Debye's computational formulae[17] were used to evaluate the Debye expressions. In the interval, $0 \leq b_1/T < 2$, the heat capacity expression is given by

$$D(x) = 1.0 + d_1 x^2 + d_2 x^4 + \ldots$$

and the enthalpy expression by

$$D(x) = (1.0 + d_1 x^2 + d_2 x^4 + \ldots + \frac{3x}{e^x - 1})/4$$

where $x = b_1/T$ and

$$d_n = \frac{(-1)^n (6n - 3) B_n}{(2n + 3)(2n)!}$$

B_n is the n-th Bernoulli number. A table of B_n and d_n is given in the Appendix. In the interval $2 \leq b_1/T < 16$

$$\int_0^x \frac{y^3 dy}{e^y - 1} = \frac{\pi^4}{15} - x^4 \sum_{n=1}^{\infty} e^{-nx} \left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right)$$

If $16 \leq b_1/T$, the heat capacity expression is given by

$$D(x) = \frac{4\pi^4}{5x^3} = 77.9272728 \, /x^3$$

and the enthalpy expression is given by

$$D(x) = \frac{\pi^4}{5x^3} = 19.4818182 \, /x^3$$

Where necessary, $e^x - 1$ was evaluated according to the relation

$$e^x - 1 = \sum_{n=1}^{\infty} x^n/n!$$

to avoid a loss of significant figures.

To test the method and the algorithm, expressions were fitted to the data of King[18] for three mixed oxides. The parameters reported by King were used as initial estimates. To demonstrate the wide temperature interval over which the method is valid, expressions were fitted to the heat capacity and enthalpy data for aluminum oxide from 0°K to 1200°K determined by the National Bureau of Standards.[19] The results are given below.

C_p ($LiFeO_2$, 51°K to 298°K) = 9.398D(366.6/T) + 15.306E(597.9/T);

(Standard deviation is 0.017 (0.14%); King's values give 0.110.)

$$C_p \ (LiAlO_2, \ 51°K \text{ to } 298°K) = 7.685D(421.1/T) + 9.823E(637.3/T) + 7.364E(1147.6/T);$$

(Standard deviation is 0.007 (0.06%); King's values give 0.088.)

$$C_p \ (NaFeO_2, \ 51°K \text{ to } 298°K) = 8.451D(257.5/T) + 9.965E(441.7/T) + 8.387E(768.3/T);$$

(Standard deviation is 0.014 (0.10%); King's values give 0.368.)

$$C_p \ (Al_2O_3, \ 0°K \text{ to } 1200°K) = 27.792D(563.99/T) + 36.925E(566.17/T) + 62.182E(956.00/T) + 7.7676E(3254.0/T);$$

(Standard deviation is 0.070 (0.10%).)

$$H_T - H_o^o \ (Al_2O_3, \ 0°K \text{ to } 1200°K) = 27.012D(565.78/T) + 36.196E(553.69/T) + 63.504E(950.78/T) + 8.5898E(3182.3/T);$$

(Standard deviation is 1.56 (0.07%).).

The parameters are not identical in the last two cases; the enthalpy expression should be considered to be the more realistic because the data on which it is based are experimental measurements, not derived values. The standard deviations reported above correspond to about 0.1 percent and are believed to be almost entirely due to statistical fluctuations in the data due to experimental error. The random distribution of data points around values determined by the Born approximation supports this conclusion.

No great significance should be attached to the results, but Shomate's heat capacity data for ammonium sulfate,[20] which show a sharp lambda point near 223°K, are satisfactorily represented below the peak by the expression

$$C_p\ ((NH_4)_2SO_4,\ 52.8°K \text{ to } 223°K) = 10.416D(135.57/T)$$
$$+ 9.3368E(331.10/T) + 28.797E(578.84/T) + 7.1632E(662.47/T)$$
$$+ 9355.7 \exp(-4.7651(223.91 - T)^{0.12344});$$

(Standard deviation is 0.112 (0.2%).).

Fitting the New Thermodynamic Expressions

The heat capacity expression which employs the new vibrational frequency distribution function developed in this work was fitted to the C_v data for NaCl of Clusius, et al.[21] and those of Morrison, et al.[22] Because the agreement of the two sets of measurements is poor above 200°K, no data from either set were taken above that temperature.

The required partial derivatives are as follows

$$\frac{\partial C_v}{\partial a_i} = \int_o^\infty \frac{(h^2\nu^2/kT^2)\ e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}\left[\left(1 - \frac{2\pi a_i^2}{N^2}(\nu - c_i)^2\right)e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)\nu}\right] d\nu$$

$$\frac{\partial C_v}{\partial c_i} = \int_o^\infty \frac{(h^2\nu^2/kT^2)\ e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}\left[\left(\frac{2\pi a_i^3}{N^2}(\nu - c_i)\right) e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2}\right] d\nu$$

$$\frac{\partial (U_T - U_o^o)}{\partial a_i} = \int_o^\infty \left[\frac{h\nu}{e^{h\nu/kT} - 1}\right]\left[e^{-\frac{\pi a_i^2}{N^2}}\left(1 - \frac{2\pi a_i^2}{N^2}(\nu - c_i)^2\right)\right] d\nu$$

$$\frac{\partial (U_T - U_o^o)}{\partial c_i} = \int_o^\infty \left[\frac{h\nu}{e^{h\nu/kT} - 1}\right]\left[\frac{2\pi a_i^3}{N^2}(\nu - c_i)\ e^{-\frac{\pi a_i^2}{N^2}(\nu - c_i)^2}\right] d\nu$$

The integrals were evaluated by Simpson's rule. The physical constants,

h, k, and N, were taken from a list of values recommended by the National Academy of Sciences - National Research Council.[23] The primitive cell, with two atoms, was used rather than the unit cell, with eight atoms, to reduce the number of parameters to be adjusted. Using Clusius' data, from three sets of initial estimates, two sets converged on the results given below. A third set led to a false solution with a higher standard error. The values of a_i and c_i are

$a_1 = 1.346 \times 10^{12}$ sec;

$c_1 = 4.965 \times 10^{12}$ sec^{-1};

$a_2 = a_3 = 0.3845 \times 10^{12}$ sec;

$c_2 = c_3 = 2.88. \times 10^{12}$ sec^{-1};

$a_4 = 0.4436 \times 10^{12}$ sec;

$c_4 = 6.166 \times 10^{12}$ sec^{-1};

$a_5 = a_6 = 0.9258 \times 10^{12}$ sec;

$c_5 = c_6 = 4.682 \times 10^{12}$ sec^{-1}

The resulting expression represents the heat capacity values with a standard deviation of 0.02 cal/mole °K. The resulting vibration frequency distribution function is shown in Figure 1. The distribution function is in good agreement with the results of Kellermann,[24,25] Neuberger,[26] Karo,[27,28] and Arase,[29] who derived it by means of lattice-theory calculations. Using Morrison's data, the following results were obtained

$a_1 = 14.16 \times 10^{12}$ sec;

$c_1 = 5.260 \times 10^{12}$ sec^{-1};

$a_2 = a_3 = 0.3082 \times 10^{12}$ sec;

$c_2 = c_3 = 2.868 \times 10^{12}$ sec^{-1}

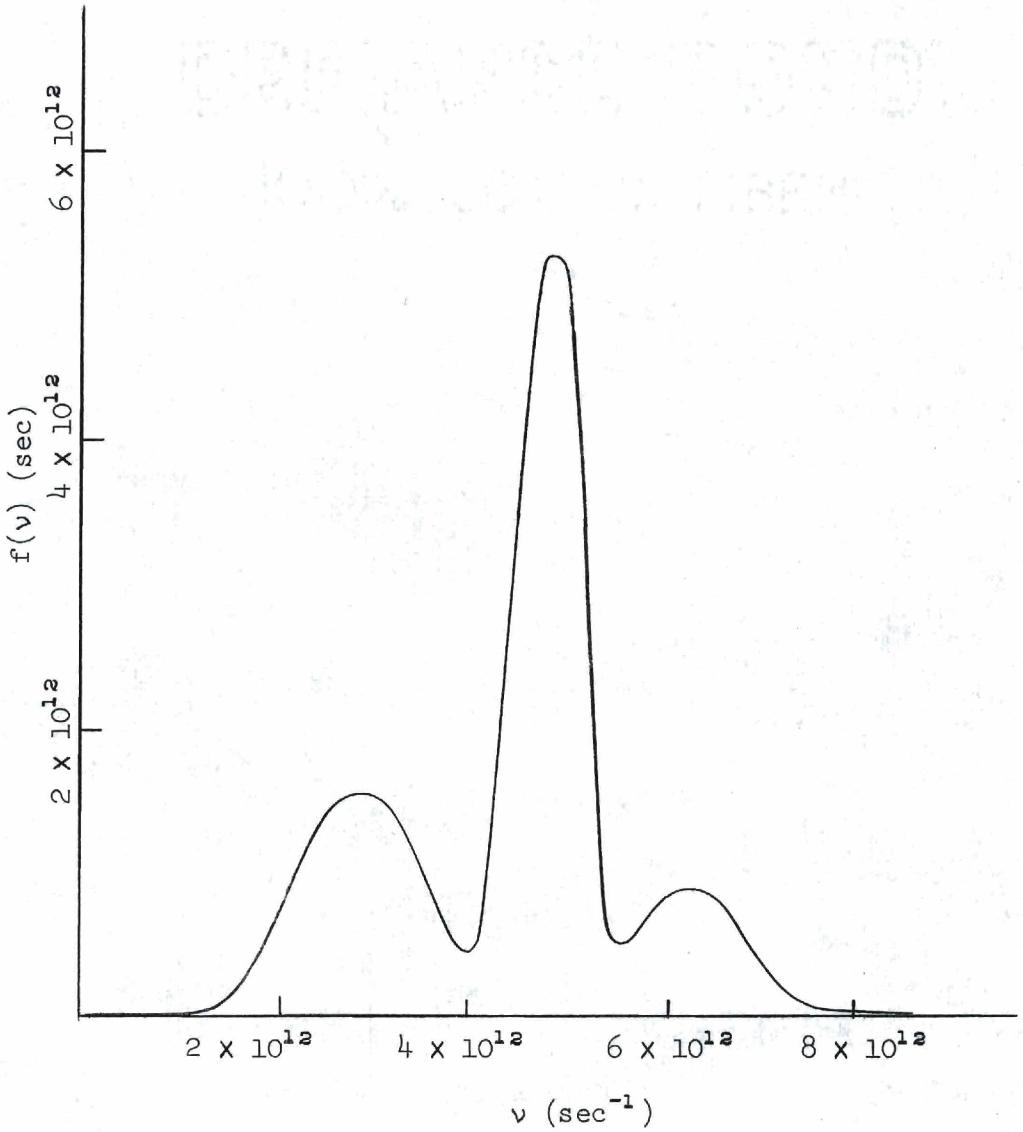

Figure 1. Vibrational Frequency Distribution Function for NaCl Derived from Calorimetric Data

$a_4 = 0.5054 \times 10^{12}$ sec;

$c_4 = 5.439 \times 10^{12}$ sec^{-1};

$a_5 = a_6 = 0.8615 \times 10^{12}$ sec;

$c_5 = c_6 = 5.038 \times 10^{12}$ sec^{-1}

The resulting expression represents the data with a standard deviation of 0.01 cal/mole °K. There are obvious differences between the two sets of results. However, because of the very low sensitivity of the heat capacity to the exact form of the vibrational frequency distribution function, the agreement should be considered to be quite good. There is particularly good agreement in the positions of the peaks in the distribution functions. The values of c_i, which represent these positions, should be compared with the infrared peaks at 2×10^{12} sec^{-1}, 4.92×10^{12} sec^{-1} (main peak), and 7.41×10^{12} sec^{-1} reported by McCubbin and Sinton.[30]

Computer Algorithms

The digital computer algorithms by which the fitting procedures just described were accomplished were written in ALGOL-60 for the Burroughs B-5500. A minimum system configuration is required. The details of the ALGOL-60 language may be found in the reports of the Working Group 2.1 of the International Federation for Information Processing, such as reference 31, and in publications of the Burroughs Corporation, such as reference 32.

The important sections of each algorithm are EVAL, MATRIX, and JORDAN. EVAL describes the evaluation of the arithmetic expression to be used to describe calorimetric data and the partial derivatives with respect to each adjustable parameter for each temperature value given. It also describes the calculation of the sum of the squares of the re-

siduals. MATRIX describes the construction of the normal matrix. JORDAN describes the solution of the equation, $(D^T\Omega D)^{-1} D^T\Omega r = c$, explained earlier. The solution is performed by Gaussian elimination with row pivots. In the third algorithm, this elimination is performed in double precision, using Lukasiewicz' Polish notation. The algebraic equivalent precedes each Polish statement as a COMMENT. LEVEN provides restart capability in case of convergence failure and applies the Levenberg correction cumulatively as needed.

Some of the important auxiliary procedures are DEBU(), EINU(), DEBC(), EINC(), and EXPT(). DEBU() and EINU() describe the evaluation of the Debye and Einstein internal energy expressions for a given value of the argument. DEBC() and EINC() describe the evaluation of the Debye and Einstein heat capacity expressions for a given value of the argument. EXPT(x) describes the evaluation of exp(x) - 1; it is used to assure accurate results for small values of the argument.

An attempt has been made to use similar or identical identifiers for similar elements of the three algorithms. Some of the more important identifiers are defined as follows:

X[]: experimental temperature data;

Y[]: experimental enthalpy or heat capacity data;

C[], RC[]: estimates of the adjustable parameter values (RC stores the values to prevent their loss due to convergence failure.);

CY[]: the value of the dependent variable (enthalpy or heat capacity) evaluated for each temperature value, using the most recent values of the adjustable parameters;

PD[,]: partial derivatives of the expression to be fitted with

respect to each adjustable parameter evaluated for each temperature value, using the most recent values of the adjustable parameters;

A[,], B[,], BH[,], BL[,]: the normal matrix (A[,] stores the matrix while operations are performed on B[,], BH[,], and BL[,] to prevent its loss in case of convergence failure. BH[,] and BL[,] are used for double-precision operations on the matrix.);

CC[]: calculated corrections to the adjustable parameters;

WT1, WT2: Levenberg constants (WT1 is used routinely and WT2 is used in case of convergence failure.);

LIM1: the fractional change in the adjustable parameters below which iteration is to be terminated;

LIM2: the fractional change in the sum of the squares of the residuals between iterations below which iteration is to be terminated;

SSQ, RSQ: the sum of the squares of the residuals (RSQ stores the value to prevent its loss due to convergence failure.);

DEB: the number of Debye terms to be included in the Born approximation;

EIN: the number of Einstein terms to be included in the Born approximation;

M: the number of adjustable parameters (M is not automatically set to 2 x (DEB + EIN) because the algorithm is also used with modified Born expressions.);

N: the number of data points to which an expression is to be fitted;

PI: pi (3.1415926);

NA: the square of Avogadro's number (3.62789×10^{47} $mole^{-2}$);

PLANCK: Planck's constant (6.62517×10^{-34} joule second);

BOLTZMANN: Boltzmann's constant (1.38044×10^{-23} joule/°K);

NU: vibrational frequency in second^{-1};

PCS: a Boolean variable which indicates whether results are to be printed after each iteration;

BOOL: a Boolean variable which indicates whether iteration should be terminated prematurely due to time restrictions (If premature termination is necessary, current values of the adjustable parameters are put out on punched cards to facilitate restarting.).

The details of the algorithms and their mode of operation are best taken from the algorithms themselves, which are given on the following pages.

DIGITAL COMPUTER ALGORITHM IN ALGOL-60 TO FIT THE BORN APPROXIMATION TO ENTHALPY OR INTERNAL ENERGY DATA

```
    BEGIN
FILE IN CARD (2, 10) ;
FILE OUT PRINT 1(2, 15) ;
FILE OUT PUNCH 0(2, 10) ;
INTEGER I ;
REAL A ;
ARRAY CB[1:30], FACT[0:29] ;
LABEL EXIT ;
      A ← FACT[0] ← 2 ;
      FOR I ← 1 STEP 1 UNTIL 29 DO
    BEGIN
      A ← A × (I + 2) ;
      FACT[I] ← A
    END ;
      FILL CB[*] WITH -0.05, 0.178571428571@-02,
          -0.551146384480@-04,  0.157828282828@-05,
          -0.433594183594@-07,  0.116252183051@-08,
          -0.307011132175@-10,  0.802819017550@-12,
          -0.208518649938@-13,  0.538989199208@-15,
          -0.138826871275@-16,  0.356140975296@-18,
          -0.914148372318@-20,  0.233946745674@-21,
          -0.597914737434@-23,  0.152647294916@-24,
          -0.389356959692@-26,  0.992383253256@-28,
          -0.252775000619@-29,  0.643506099156@-31,
          -0.163745028175@-32,  0.416492936375@-34,
          -0.105899458558@-35,  0.269181526196@-37,
          -0.684034557542@-39,  0.173782316636@-40,
          -0.441407159456@-42,  0.112095789522@-43,
          -0.284619011689@-45,  0.722554501601@-47 ;
    BEGIN
ARRAY A, B[0:8,0:9], X, Y, CY, D[0:150], PD[0:8,0:150],
      C, CC, RC[0:8] ;
INTEGER E, F, G, H, I, J, K, L, M, N, JJ, JM, DEB, EIN, MM,
      CT, CTLIM ;
REAL EXT, SSQ, BDW, DDW, EBW, WT1, WT2, LIM1, LIM2, RSQ, SE,
      RB ;
BOOLEAN V, BOOL, PCS ;
LABEL START, MATRIX, JORDAN, PRNT, LEVEN ;
LIST  RES1 (FOR I ← 1 STEP 1 UNTIL M DO [I, C[I]]),
      RES3 (FOR I ← 1 STEP 1 UNTIL N DO [X[I], Y[I], CY[I],
        D[I]]) ;
FORMAT FORM1 (X10,"C[",I2,"] =",E16.8),
      FORM2 (/X10,"STANDARD ERROR IS",E16.8///),
      FORM3 (X8,4E16.8),
      HEAD (/X17,"T",X11,"ENTHALPY     CALC. ENTHALPY    ",
        "DIFFERENCE"/),
      INITIAL (X10,"INITIAL VALUES"//),
      FINAL (X10,"FINAL VALUES"//),
```

```
      CORR (/X10,"LEVENBERG CORRECTION APPLIED"//),
      DATA1 (4I5),
      DATA2 (F8.2,F12.4),
      DATA3 (F26.12),
      ERROR (/X10,"DESIGN TOLERANCES WERE NOT REACHED."//) ;
REAL PROCEDURE EXPT (W) ;
      VALUE W ;
      REAL W ;
    BEGIN
      REAL A, B, C, EXT ;
      INTEGER I ;
      IF ABS (W) < 0.2 THEN
    BEGIN
      I ← 0 ;
      A ← W × W ;
      B ← A / 2 ;
      C ← ABS (1@-10 × W) ;
      EXT ← W + B ;
      WHILE ABS (B) > C DO
    BEGIN
      I ← I + 1 ;
      A ← A × W ;
      B ← A / FACT[I] ;
      EXT ← EXT + B
    END
    END
      ELSE EXT ← EXP(W) - 1 ;
      EXPT ← EXT
    END ;
REAL PROCEDURE DEBU (W) ;
      VALUE W ;
      REAL W ;
    BEGIN
      REAL A, B, C, D, F, G, H, V, Y, DU ;
      INTEGER N ;
      FORMAT ERROR ("ARGUMENT OF DEBU() IS NEGATIVE.") ;
      EXT ← IF W > 79 THEN 2@34 ELSE EXPT(W) ;
      F ← W × W ;
      IF W ≥ 30 THEN DU ← 19.4818182067 / (W × F) ELSE
      IF W ≥ 4 AND W < 30 THEN
    BEGIN
      C ← W × F ;
      D ← F × F ;
      G ← H ← 1 / (EXT + 1) ;
      V ← (6 × W + 3 × F + C + 6) × G / D ;
      Y ← 6.4939394022 / D - V ;
      N ← 2 ;
      WHILE V > 1@-11 DO
    BEGIN
      A ← N × W ;
      B ← A × A ;
      C ← A × B ;
```

```
      D ← B × B ;
      G ← G × H ;
      V ← (6 × A + 3 × B + C + 6) × G / D ;
      Y ← Y - V ;
      N ← N + 1
    END ;
      DU ← 3 × Y × W ;
    END ELSE
      IF W ≥ 0 AND W < 4 THEN
    BEGIN
      B ← A ← 1 ;
      N ← 0 ;
      DO
    BEGIN
      N ← N + 1 ;
      A ← A × F ;
      B ← A × CB[N] + B ;
      N ← N + 1 ;
      A ← A × F ;
      C ← A × CB[N] ;
      B ← B + C
    END UNTIL C < 1@-9 ;
      DU ← (3 × W / EXT + B) / 4 ;
    END
      ELSE
    BEGIN
      DU ← 1 ;
      WRITE (PRINT, ERROR)
    END ;
      DERU ← DU
    END ;
REAL PROCEDURE EINU (W) ;
      VALUE W ;
      REAL W ;
    BEGIN
      REAL EU ;
      FORMAT ERROR ("ARGUMENT OF EINU() IS NEGATIVE.") ;
      EXT ← IF W > 79 THEN 2@34 ELSE EXPT(W) ;
      IF W ≥ 1@-10 THEN EU ← W / EXT ELSE
      IF W ≥ 0 AND W < 1@-10 THEN EU ← 1
      ELSE
    BEGIN
      EU ← 1 ;
      WRITE (PRINT, ERROR)
    END ;
      EINU ← EU
    END ;
PROCEDURE EVAL ;
    BEGIN
      SS0 ← 0 ;
      FOR I ← 1 STEP 1 UNTIL N DO
    BEGIN
```

```
      CY[I] ← 0 ;
      FOR J ← 1 STEP 1 UNTIL DEB DO
    BEGIN
      JJ ← J + J ;
      JM ← JJ - 1 ;
      DDW ← X[I] × DEBU (C[JJ] / X[I]) ;
      CY[I] ← DDW × C[JM] + CY[I] ;
      PD[JM,I] ← DDW ;
COMMENT EXT IS GENERATED IN THE DEBU() PROCEDURE. ;
      PD[JJ,I] ← 3 × C[JM] × (1 / EXT - DDW / C[JJ])
    END ;
      FOR J ← DEB + 1 STEP 1 UNTIL E DO
    BEGIN
      JJ ← J + J ;
      JM ← JJ - 1 ;
      BDW ← EINU (C[JJ] / X[I]) ;
      DDW ← X[I] × BDW ;
      CY[I] ← DDW × C[JM] + CY[I] ;
      PD[JM,I] ← DDW ;
COMMENT EXT IS GENERATED IN THE EINU() PROCEDURE ;
      PD[JJ,I] ← C[JM] × (1 - BDW × (EXT + 1)) / EXT
    END ;
      D[I] ← Y[I] - CY[I] ;
      SSQ ← SSQ + D[I] × D[I]
    END
    END ;
      PCS ← TRUE ;
      CTLIM ← 100 ;
      WT1 ← 1.00001 ;
      WT2 ← 1.0001 ;
      LIM1 ← LIM2 ← 10-8 ;
  START: READ (CARD, DATA1, DEB, EIN, M, N)[EXIT] ;
      READ (CARD, DATA2, FOR I ← 1 STEP 1 UNTIL N DO
        [X[I], Y[I]]) ;
      READ (CARD, DATA3, FOR I ← 1 STEP 1 UNTIL M DO C[I]) ;
      CLOSE (CARD,RELEASE) ;
      E ← DEB + EIN ;
      G ← N - M ;
      H ← M + 1 ;
      CT ← 0 ;
      EVAL ;
      RSQ ← SSQ ;
      SE ← SQRT (SSQ / G) ;
      WRITE (PRINT [PAGE]) ;
      WRITE (PRINT, INITIAL) ;
      WRITE (PRINT, FORM1, RES1) ;
      WRITE (PRINT, FORM2, SE) ;
      WRITE (PRINT, HEAD) ;
      WRITE (PRINT, FORM3, RES3) ;
      WRITE (PRINT [PAGE]) ;
  MATRIX:  FOR I ← 1 STEP 1 UNTIL M DO
    BEGIN
```

```
    FOR J ← I STEP 1 UNTIL M DO
  BEGIN
    A[I,J] ← 0 ;
    FOR K ← 1 STEP 1 UNTIL N DO
        A[I,J] ← PD[I,K] × PD[J,K] + A[I,J]
  END ;
    A[I,H] ← 0 ;
    FOR K ← 1 STEP 1 UNTIL N DO A[I,H] ← PD[I,K] × D[K] +
      A[I,H]
  END ;
    FOR I ← 2 STEP 1 UNTIL M DO
    FOR J ← 1 STEP 1 UNTIL I-1 DO
        A[I,J] ← A[J,I] ;
    FOR I ← 1 STEP 1 UNTIL M DO A[I,I] ← WT1 × A[I,I] ;
    CT ← CT + 1 ;
JORDAN: BOOL ← CT > CTLIM ;
    IF BOOL THEN GO TO PRNT ;
    FOR I ← 1 STEP 1 UNTIL M DO
    FOR J ← 1 STEP 1 UNTIL H DO
        B[I,J] ← A[I,J] ;
    FOR K ← H STEP -1 UNTIL 1 DO
  BEGIN
    RB ← 0 ;
    FOR I ← 2 STEP 1 UNTIL K DO
  BEGIN
    IF ABS (B[I-1,1]) > RB THEN
  BEGIN
    F ← I - 1 ;
    RB ← ABS (B[F,1])
  END
  END ;
    IF F ≠ 1 THEN
  BEGIN
    FOR J ← 1 STEP 1 UNTIL K DO
  BEGIN
    RB ← B[F,J] ;
    B[F,J] ← B[1,J] ;
    B[1,J] ← RB
  END
  END ;
    FOR I ← 1 STEP 1 UNTIL M DO CC[I] ← B[I,1] ;
    FOR J ← 2 STEP 1 UNTIL K DO
  BEGIN
    RB ← B[1,J] / CC[1] ;
    FOR I ← 2 STEP 1 UNTIL M DO
      B[I-1,J-1] ← B[I,J] - RB × CC[I] ;
    B[M,J-1] ← RB
  END
  END ;
    FOR I ← 1 STEP 1 UNTIL M DO
  BEGIN
    RC[I] ← C[I] ;
```

```
      C[I] ← C[I] + CC[I]
    END ;
      EVAL ;
      IF SSQ > RSQ THEN GO TO LEVEN ;
      IF PCS THEN
    BEGIN
      SE ← SQRT (SSQ / G) ;
      WRITE (PRINT, FORM1, RES1) ;
      WRITE (PRINT, FORM2, SE)
    END ;
      V ← FALSE ;
      I ← 1 ;
      DO
    BEGIN
      V ← ABS (CC[I] / C[I]) > LIM1 ;
      I ← I + 1
    END UNTIL V OR I > M ;
      BOOL ← CT > CTLIM ;
      IF (V OR (RSQ - SSQ) / SSQ > LIM2) AND  NOT BOOL THEN
    BEGIN
      RSQ ← SSQ ;
      GO TO MATRIX
    END ;
PRNT: WRITE (PRINT [PAGE]) ;
      IF NOT PCS THEN SE ← SQRT (SSQ / G) ;
      WRITE (PRINT, FINAL) ;
      IF BOOL THEN WRITE (PRINT, ERROR) ;
      WRITE (PRINT, FORM1, RES1) ;
      WRITE (PRINT, FORM2, SE) ;
      WRITE (PRINT, HEAD) ;
      WRITE (PRINT, FORM3, RES3) ;
      WRITE (PUNCH, DATA3, FOR I ← 1 STEP 1 UNTIL M DO C[I]) ;
      GO TO EXIT ;
LEVEN: FOR I ← 1 STEP 1 UNTIL M DO
    BEGIN
      C[I] ← RC[I] ;
      A[I,I] ← WI2 × A[I,I]
    END ;
      WRITE (PRINT, CORR) ;
      GO TO JORDAN
    END ;
EXIT: END.
```

DIGITAL COMPUTER ALGORITHM IN ALGOL-60 TO FIT THE BORN APPROXIMATION TO HEAT CAPACITY DATA

```
    BEGIN
FILE IN CARD (2, 10) ;
FILE OUT PRINT 1(2, 15) ;
FILE OUT PUNCH 0(2, 10) ;
INTEGER I ;
REAL A ;
ARRAY CB[1:30], FACT[0:29] ;
LABEL EXIT ;
      A ← FACT[0] ← 2 ;
      FOR I ← 1 STEP 1 UNTIL 29 DO
    BEGIN
      A ← A × (I + 2) ;
      FACT[I] ← A
    END ;
      FILL CB[*] WITH -0.05, 0.1785714285710-02,
          -0.5511463844800-04,  0.1578282828280-05,
          -0.4335941835940-07,  0.1162521830510-08,
          -0.3070111321750-10,  0.8028190175500-12,
          -0.2085186499380-13,  0.5389891992080-15,
          -0.1388268712750-16,  0.3566140975260-18,
          -0.9141483723180-20,  0.2339467456740-21,
          -0.5979147374340-23,  0.1526472949160-24,
          -0.3893569596920-26,  0.9923832532560-28,
          -0.2527750006190-29,  0.6435060991560-31,
          -0.1637450281750-32,  0.4164929363750-34,
          -0.1058994585580-35,  0.2691815261260-37,
          -0.6840345575420-39,  0.1737823166360-40,
          -0.4414071594560-42,  0.1120957895220-43,
          -0.2846190116890-45,  0.7225545016010-47 ;
    BEGIN
ARRAY A, B[0:8,0:91, X, Y, CY, D[0:150], PD[0:8,0:150],
      C, CC, RC[0:8] ;
INTEGER E, F, G, H, I, J, K, L, M, N, JJ, JM, DEB, EIN, MM ;
REAL EX1, SSQ, BDW, DDW, EBW, TTC, PT1, WT1, WT2, LIM1,
      LIM2, RSQ, SE, RR, W2, TM, TMLIM ;
BOOLEAN V, BOOL ;
LABEL START, MATRIX, JORDAN, PRNT, LEVEN ;
LIST  RES1 (FOR I ← 1 STEP 1 UNTIL M DO [I, C[I]]),
      RES3 (FOR I ← 1 STEP 1 UNTIL N DO [X[I], Y[I], CY[I],
        D[I]]) ;
FORMAT FORM1 (X10,"C(",I2,") =",E16.8),
      FORM2 (/X10,"STANDARD ERROR IS",E16.8///),
      FORM3 (X8,4E16.8),
      HEAD (/X17,"T",X14,"CP",X11,"CALC. CP",X7,
        "DIFFERENCE"/),
      INITIAL (X10,"INITIAL VALUES"//),
      FINAL (X10,"FINAL VALUES"//),
      CURR (/X10,"LEVENBERG CORRECTION APPLIED"//),
```

```
      DATA3 (F26.12),
      ERROR (/X10,"DESIGN TOLERANCES WERE NOT REACHED."//) ;
FORMAT IN DATA1 (4I5), DATA2 (X7,F8.2,F8.3) ;
REAL PROCEDURE EXPT (W) ;
      VALUE W ;
      REAL W ;
    BEGIN
      REAL A, B, EXT ;
      INTEGER I ;
      IF W < -21 THEN EXT ← -1 ELSE
      IF W < 1@-10 AND W ≥ -1@-10 THEN EXT ← W ELSE
      IF W < 2 AND W ≥ 1@-10 THEN
    BEGIN
      A ← EXT ← W ;
      I ← 0 ;
      DO
    BEGIN
      A ← A × W ;
      B ← A / FACT[I] ;
      EXT ← EXT + B ;
      I ← I + 1
    END UNTIL B < 1@-10 ;
    END
      ELSE EXT ← EXP(W) - 1 ;
      EXPT ← EXT
    END ;
REAL PROCEDURE DEBC (W) ;
      VALUE W ;
      REAL W ;
COMMENT  REAL VARIABLES, EXT AND W2, MUST BE DECLARED
      GLOBAL TO THIS PROCEDURE. ;
    BEGIN
      REAL A, B, C, D, E, F, Q, V, Y, DC ;
      INTEGER N ;
      FORMAT ERROR ("ARGUMENT OF DEBC() IS NEGATIVE.") ;
      IF W > 40 THEN DC ← 0 ELSE
    BEGIN
      EXT ← EXPT (W) ;
      F ← W × W ;
      W2 ← F ;
      E ← W × F ;
      IF W ≥ 30 THEN DC ← 77.927273 / E ELSE
      IF W ≥ 4 AND W < 30 THEN
    BEGIN
      Q ← W × E ;
      Y ← 6.4939394 ;
      N ← 1 ;
      DO
    BEGIN
      A ← N × W ;
      B ← A × A ;
      C ← A × B ;
```

```
      D ← B × B ;
      V ← (1/A + 3/B + 6/C + 6/D) × Q × EXP(-A) ;
      Y ← Y - V ;
      N ← N + 1
    END UNTIL V < 1@-9 ;
      DC ← 12 × Y / E - 3 × W / EXT ;
    END ELSE
      IF W ≥ 0 AND W < 4 THEN
    BEGIN
      DC ← A ← 1 ;
      N ← 0 ;
      DO
    BEGIN
      N ← N + 1 ;
      A ← A × F ;
      DC ← A × CB[N] + DC ;
      N ← N + 1 ;
      A ← A × F ;
      C ← A × CB[N] ;
      DC ← DC + C
    END UNTIL C < 1@-9 ;
    END
      ELSE
    BEGIN
      DC ← 1 ;
      WRITE (PRINT, ERROR)
    END
    END ;
      DERC ← DC
    END ;
REAL PROCEDURE EINC (W) ;
      VALUE W ;
      REAL W ;
COMMENT  A REAL VARIABLE, EXT, MUST BE DECLARED GLOBAL TO
      THIS PROCEDURE. ;
    BEGIN
      REAL EC ;
      FORMAT ERROR ("ARGUMENT OF EINC() IS NEGATIVE.") ;
      IF W > 20 THEN EC ← 0 ELSE
    BEGIN
      EXT ← EXPT (W) ;
      IF W ≥ 1@-4 THEN EC ← W × W × (EXT + 1) / (EXT × EXT) ELSE
      IF W ≥ 0 AND W < 1@-4 THEN EC ← 1
      ELSE
    BEGIN
      EC ← 1 ;
      WRITE (PRINT, ERROR)
    END
    END ;
      EINC ← EC
    END ;
PROCEDURE EVAL ;
```

```
    BEGIN
      SSQ ← 0 ;
      FOR I ← 1 STEP 1 UNTIL N DO
    BEGIN
      CY[I] ← 0 ;
      FOR J ← 1 STEP 1 UNTIL DEB DO
    BEGIN
      JJ ← J + J ;
      JM ← JJ - 1 ;
      BDW ← C[JJ] / X[I] ;
      DDW ← DEBC (BDW) ;
      CY[I] ← DDW × C[JM] + CY[I] ;
      PD[JM,I] ← DDW ;
COMMENT W2 AND EXT ARE EVALUATED IN THE DEBC() PROCEDURE ;
      PD[JJ,I] ← 3 × C[JM] × ( W2 × (EXT + 1) / (EXT × EXT)
          - DDW) / CC[JJ]
    END ;
      FOR J ← DEB + 1 STEP 1 UNTIL E DO
    BEGIN
      JJ ← J + J ;
      JM ← JJ - 1 ;
      BDW ← C[JJ] / X[I] ;
      DDW ← EINC (BDW) ;
      CY[I] ← DDW × C[JM] + CY[I] ;
      PD[JM,I] ← DDW ;
COMMENT EXT IS EVALUATED IN THE EINC() PROCEDURE ;
      PD[JJ,I] ← C[JM] × (1/X[I] + 2/C[JJ] - 2 × (EXT + 1) /
          (EXT × X[I])) × DDW
    END ;
      D[I] ← Y[I] - CY[I] ;
      SSQ ← SSQ + D[I] × D[I]
    END
    END ;
      TM ← TIME (2) ;
      TMLIM ← 10 ;
      WT1 ← WT2 ← 1.02 ;
      LIM1 ← LIM2 ← 1@-6 ;
  START: READ (CARD, DATA1, DEB, EIN, M, N)[EXIT] ;
      READ (CARD, DATA2, FOR I ← 1 STEP 1 UNTIL N DO
        [X[I], Y[I]]) ;
      READ (CARD, DATA3, FOR I ← 1 STEP 1 UNTIL M DO C[I]) ;
      E ← DEB + EIN ;
      G ← N - M ;
      H ← M + 1 ;
      MM ← M - 1 ;
      EVAL ;
      RSQ ← SSQ ;
      SE ← SQRT (SSQ / G) ;
      WRITE (PRINT [PAGE]) ;
      WRITE (PRINT, INITIAL) ;
      WRITE (PRINT, FORM1, RES) ;
      WRITE (PRINT, FORM2, SE) ;
```

```
    WRITE (PRINT, HEAD) ;
    WRITE (PRINT, FORM3, RES3) ;
    WRITE (PRINT [PAGE]) ;
MATRIX:  FOR I ← 1 STEP 1 UNTIL M DO
  BEGIN
    FOR J ← I STEP 1 UNTIL M DO
  BEGIN
    A[I,J] ← 0 ;
    FOR K ← 1 STEP 1 UNTIL N DO A[I,J] ← PD[I,K] × PD[J,K]
      + A[I,J]
  END ;
    A[I,H] ← 0 ;
    FOR K ← 1 STEP 1 UNTIL N DO A[I,H] ← PD[I,K] × D[K] +
      A[I,H]
  END ;
    FOR I ← 2 STEP 1 UNTIL M DO
    FOR J ← 1 STEP 1 UNTIL I-1 DO
        A[I,J] ← A[J,I] ;
    FOR I ← 1 STEP 1 UNTIL M DO A[I,I] ← WT1 × A[I,I] ;
JORDAN: BOOL ← (TIME (2) - TM) / 3600 > TMLIM ;
    IF BOOL THEN GO TO PRNT ;
    FOR I ← 1 STEP 1 UNTIL M DO
    FOR J ← 1 STEP 1 UNTIL H DO
        B[I,J] ← A[I,J] ;
    FOR K ← H STEP -1 UNTIL 1 DO
  BEGIN
    RB ← 0 ;
    FOR I ← 2 STEP 1 UNTIL K DO
  BEGIN
    IF ABS (B[I-1,1]) > RB THEN
  BEGIN
    F ← I - 1 ;
    RB ← ABS (B[F,1])
  END
  END ;
    IF F ≠ 1 THEN
  BEGIN
    FOR J ← 1 STEP 1 UNTIL K DO
  BEGIN
    RB ← B[F,J] ;
    B[F,J] ← B[1,J] ;
    B[1,J] ← RB
  END
  END ;
    FOR I ← 1 STEP 1 UNTIL M DO CC[I] ← B[I,1] ;
    FOR J ← 2 STEP 1 UNTIL K DO
  BEGIN

    RB ← B[1,J] / CC[1] ;
    FOR I ← 2 STEP 1 UNTIL M DO B[I-1,J-1] ← B[I,J] -
      RB × CC[I] ;
    B[M,J-1] ← RB
  END
```

```
    END ;
      FOR I ← 1 STEP 1 UNTIL M DO
    BEGIN
      RC[I] ← C[I] ;
      C[I] ← C[I] + CC[I]
    END ;
      EVAL ;
      IF SSQ > RSQ THEN GO TO LEVEN ;
      SE ← SQRT (SSQ / G) ;
      WRITE (PRINT, FORM1, RES1) ;
      WRITE (PRINT, FORM2, SE) ;
      V ← FALSE ;
      I ← 1 ;
      DO
    BEGIN
      V ← ABS (CC[I] / C[I]) > LIM1 ;
      I ← I + 1
    END UNTIL V OR I > M ;
      BOOL ← (TIME (2) - TM) / 3600 > TMLIM ;
      IF (V OR (RSQ - SSQ) / SSQ > LIM2) AND  NOT BOOL THEN
    BEGIN
      RSQ ← SSQ ;
      GO TO MATRIX
    END ;
PRNT: WRITE (PRINT [PAGE]) ;
      WRITE (PRINT, FINAL) ;
      IF BOOL THEN WRITE (PRINT, ERROR) ;
      WRITE (PRINT, FORM1, RES1) ;
      WRITE (PRINT, FORM2, SE) ;
      WRITE (PRINT, HEAD) ;
      WRITE (PRINT, FORM3, RES3) ;
      WRITE (PUNCH, DATA3, FOR I ← 1 STEP 1 UNTIL M DO C[I]) ;
      GO TO START ;
LEVEN: FOR I ← 1 STEP 1 UNTIL M DO
    BEGIN
      C[I] ← RC[I] ;
      A[I,I] ← WT2 × A[I,I]
    END ;
      WRITE (PRINT, CORR) ;
      GO TO JORDAN
    END ;
EXIT: END.
```

DIGITAL COMPUTER ALGORITHM IN ALGOL-60 TO FIT A NEW APPROXIMATE CALORIMETRIC EXPRESSION TO HEAT CAPACITY DATA

```
    BEGIN
FILE IN CARD (1,10) ;
FILE OUT PRINT 1(1,15) ;
FILE OUT PUNCH 0(1,10) ;
REAL ARRAY PD[0:8,0:150], X,Y,CY,D[0:150], A,BH,BL[0:9,0:9],
      Q[0:3,0:8], C,CC,RC,CL[0:8], PA,FN[0:41] ;
INTEGER E,F,G,H,I,J,K,L,M,N,CT,CTLIM ;
REAL SSQ,WT1,WT2,LIM1,LIM2,RSQ,SE,RB,PLANCK,BOLTZMANN,PI,NA,
      NB,SB ;
BOOLEAN V, BOOL, PCS ;
LABEL START, MATRIX, JORDAN, PRNT, LEVEN, EXIT ;
LIST  RES1 (FOR I := 1 STEP 1 UNTIL M DO [I,C[I]]),
      RES3 (FOR I := 1 STEP 1 UNTIL N DO [X[I],Y[I],CY[I],
        D[I]]) ;
FORMAT FORM1 (X10,"C[",I2,"] =",E16.8),
      FORM2 (/X10,"STANDARD ERROR IS",E16.8///),
      FORM3 (X8,4E16.8),
      ERROR (/X10,"DESIGN TOLERANCES WERE NOT REACHED."//),
      HEAD (/X17,"T",X14,"CV",X11,"CALC. CV       ",
        "DIFFERENCE"/),
      INITIAL (X10,"INITIAL VALUES"//),
      FINAL (X10,"FINAL VALUES"//),
      CURR (/X10,"LEVENBERG CORRECTION APPLIED"//),
      DATA1 (2I5),
      DATA2 (2F9.4),
      DATA3 (E17.10) ;
REAL PROCEDURE EXPT (X) ;
      VALUE X ;
      REAL X ;
    BEGIN
      REAL A,C,I,EXT ;
      A := X × X / 2 ;
      EXT := X + A ;
      C := ABS(1@-10 × X) ;
      I := 2 ;
      WHILE A > C DO
    BEGIN
      I := I + 1 ;
      A := A × X / I ;
      EXT := EXT + A ;
      I := I + 1 ;
      A := A × X / I ;
      EXT := EXT + A
    END ;
      EXPT := EXT
    END ;
PROCEDURE EVAL ;
    BEGIN
```

```
    REAL A,B,F,G,R,S,T,U,V,W,NU,HKT ;
    SSQ := 0 ;
    FOR I := 1,3 DO PA[I] := -PI × C[I] × C[I] / NA ;
    FOR I := 2,4 DO PA[I] := -PI × C[I] × C[I] / NB ;
    FOR I := 1 STEP 1 UNTIL N DO
  BEGIN
    NU := 0 ;
    HKT := PLANCK / (BOLTZMANN × X[I]) ;
    W := EXP(2@10 × HKT) ;
    FN[3] := FN[2] := FN[1] := 0 ;
    FOR J := 1,2,3,4 DO
  BEGIN
    L := J + 4 ;
    A := PA[J] × C[L] ;
    B := A × C[L] ;
    F := 2 × A × C[J] ;
    G := BOLTZMANN × EXP(B) ;
    Q[1,J] := G × (2 × B + 1) ;
    Q[3,J] := Q[2,J] := 0 ;
    Q[1,L] := -F × G ;
    Q[3,L] := Q[2,L] := 0 ;
    FN[1] := G × C[J] + FN[1]
  END ;
    G := 1 ;
    DO
  BEGIN
    FOR E := 2,3 DO
  BEGIN
    NU := NU + 2@10 ;
    A := NU × HKT ;
    G := G × W ;
    F := IF A > 0.2 THEN G - 1 ELSE EXPT(A) ;
    F := F × F ;
    A := A × A × BOLTZMANN × G / F ;
    FOR J := 1,2,3,4 DO
  BEGIN
    L := J + 4 ;
    R := NU - C[L] ;
    S := R × PA[J] ;
    T := R × S ;
    IF T > -15 THEN
  BEGIN
    U := A × EXP(T) ;
    V := C[J] × U ;
    Q[E,J] := (2 × T + 1) × U + Q[E,J] ;
    Q[F,L] := -2 × S × V + Q[F,L] ;
    FN[E] := V + FN[E]
  END
  END
  END
  END
    UNTIL NU > 1000@10 ;
```

```
    NU := NU + 2@10 ;
    A := NU × HKT ;
    G := G × W ;
    F := IF A > 0.2 THEN G - 1 ELSE EXPT(A) ;
    F := F × F ;
    A := A × A × BOLTZMANN × G / F ;
    FOR J := 1,2,3,4 DO
  BEGIN
    L := J + 4 ;
    R := NU - C[L] ;
    S := R × PA[J] ;
    T := R × S ;
    U := A × EXP(T) ;
    V := C[J] × U ;
    Q[1,J] := (2 × T + 1) × U + Q[1,J] ;
    Q[1,L] := -2 × S × V + Q[1,L] ;
    FN[1] := V + FN[1]
  END ;
    FOR J := 1,2,3,4,5,6,7,8 DO
    PD[J,I] := 2@10 × (Q[1,J] + 4 × Q[2,J] + 2 × Q[3,J])/3;
    CY[I] := 2@10 × (FN[1] + 4 × FN[2] + 2 × FN[3]) / 3 ;
    D[I] := Y[I] - CY[I] ;
    SSQ := D[I] × D[I] + SSQ
  END
  END ;
    PCS := TRUE ;
    CTLIM := 3 ;

    WT1 := 3 ;
    WT2 := 1,5 ;
    LIM1 := LIM2 := 1@-8 ;
    PI := 3.1415926 ;
    NA := 3.62789@47 ;
    NB := 1.451158@48 ;
    PLANCK := 6.62517@-34 ;
    BOLTZMANN := 1.38044@-23 ;
START: READ (CARD,DATA1,M,N)[EXIT] ;
    READ (CARD,DATA2,FOR I := 1 STEP 1 UNTIL N DO
      [X[I],Y[I]]) ;
    READ (CARD,DATA3,FOR I := 1 STEP 1 UNTIL M DO C[I]) ;
    CLOSE (CARD,RELEASE) ;
    G := N - M ;
    H := M + 1 ;
    CT := 0 ;
    EVAL ;
    RSQ := SSQ ;
    SE := SQRT(SSQ / G) ;
    WRITE (PRINT [PAGE]) ;
    WRITE (PRINT,INITIAL) ;
    WRITE (PRINT,FORM1,RES1) ;
    WRITE (PRINT,FORM2,SE) ;
    WRITE (PRINT,HEAD) ;
    WRITE (PRINT,FORM3,RES3) ;
```

```
    WRITE (PRINT [PAGE]) ;
MATRIX:  FOR I := 1 STEP 1 UNTIL M DO
  BEGIN
    FOR J := I STEP 1 UNTIL M DO
  BEGIN
    A[I,J] := 0 ;
    FOR K := 1 STEP 1 UNTIL N DO
    A[I,J] := PD[I,K] × PD[J,K] + A[I,J]
  END ;
    A[H,I] := 0 ;
    FOR K := 1 STEP 1 UNTIL N DO A[H,I] := PD[I,K] × D[K] +
      A[H,I]
  END ;
    FOR I := 2 STEP 1 UNTIL M DO
    FOR J := 1 STEP 1 UNTIL I-1 DO
        A[I,J] := A[J,I] ;
    FOR I := 1 STEP 1 UNTIL M DO A[I,I] := WT1 × A[I,I] ;
    CT := CT + 1 ;
JORDAN: BOOL := CT > CTLIM ;
    IF BOOL THEN GO TO PRNT ;
    FOR I := 1 STEP 1 UNTIL H DO
    FOR J := 1 STEP 1 UNTIL H DO
        BH[I,J] := A[I,J] ;
    K := 1 ;
    L := 0 ;
    FOR E := 2 STEP 1 UNTIL H DO
  BEGIN
    RB := ABS(BH[K,K]) ;
    F := K ;
    FOR J := E STEP 1 UNTIL M DO
  BEGIN
    SB := ABS(BH[J,K]) ;
    IF SB > RB THEN
  BEGIN
    F := J ;
    RB := SB
  END
  END ;
    IF F ≠ K THEN
  BEGIN
    RB := BH[H,F] ;
    SB := BL[H,F] ;
    BH[H,F] := BH[H,K] ;
    BL[H,F] := BL[H,K] ;
    BH[H,K] := RB ;
    BL[H,K] := SB ;
    FOR J := 1 STEP 1 UNTIL H DO
  BEGIN
    RB := BH[F,J] ;
    SB := BL[F,J] ;
    BH[F,J] := BH[K,J] ;
    BL[F,J] := BL[K,J] ;
```

```
  BH[K,J] := RB ;
  BL[K,J] := SB
END
END ;
  COMMENT
  FOR I := K STEP 1 UNTIL H DO
  FOR J := 1 STEP 1 UNTIL L DO
  BH[I,K] := BH[I,K] - BH[J,K] × BH[I,J] ;
  FOR I := K STEP 1 UNTIL H DO
  FOR J := 1 STEP 1 UNTIL L DO
  DOUBLE (BH[I,K],BL[I,K],BH[J,K],BL[J,K],
      BH[I,J],BL[I,J],×,-,:=,BH[I,K],BL[I,K]) ;
  COMMENT
  FOR J := E STEP 1 UNTIL H DO
  BH[K,J] := BH[J,K] / BH[K,K] ;
  FOR J := E STEP 1 UNTIL H DO
  DOUBLE (BH[J,K],BL[J,K],BH[K,K],BL[K,K],
      /,:=,BH[K,J],BL[K,J]) ;
  L := K ;
  K := E
END ;
  CC[M] := BH[M,H] ;
  CL[M] := BL[M,H] ;
  K := M ;
  FOR I := M-1 STEP -1 UNTIL 1 DO
BEGIN
  SB := RB := 0 ;
  COMMENT
  FOR J := M STEP -1 UNTIL K DO
  RB := CC[J] × BH[I,J] + RB ;
  FOR J := M STEP -1 UNTIL K DO
  DOUBLE (CC[J],CL[J],BH[I,J],BL[I,J],×,
      RB,SB,+,:=,RB,SB) ;
  COMMENT
  CC[I] := BH[I,H] - RB ;
  DOUBLE (BH[I,H],BL[I,H],RB,SB,-,:=,CC[I],CL[I]) ;
  K := I
END ;
  FOR I := 1 STEP 1 UNTIL M DO
BEGIN
  RC[I] := C[I] ;
  C[I] := C[I] + CC[I]
END ;
  EVAL ;
  IF SSQ > RSQ THEN GO TO LEVEN ;
  IF PCS THEN
BEGIN
  SE := SQRT(SSQ / G) ;
  WRITE (PRINT,FORM1,RES1) ;
  WRITE (PRINT,FORM2,SE)
END ;
  V := FALSE ;
```

```
    I := 1 ;
    DO
  BEGIN
    V := ABS(CC[I] / C[I]) > LIM1 ;
    I := I + 1
  END
    UNTIL V OR I > M ;
    BOOL := CT > CTLIM ;
    IF SSQ = 0 THEN GO TO PRNT ;
    IF (V OR (RSQ - SSQ) / SSQ > LIM2) AND NOT BOOL THEN
  BEGIN
    RSQ := SSQ ;
    GO TO MATRIX
  END ;
PRNT: WRITE (PRINT [PAGE]) ;
    IF NOT PCS THEN SE := SQRT(SSQ / G) ;
    WRITE (PRINT,FINAL) ;
    IF BOOL THEN WRITE (PRINT,ERROR) ;
    WRITE (PRINT,FORM1,RES1) ;
    WRITE (PRINT,FORM2,SE) ;
    WRITE (PRINT,HEAD) ;
    WRITE (PRINT,FORM3,RES3) ;
    WRITE (PUNCH,DATA3,FOR I := 1 STEP 1 UNTIL M DO C[I]) ;
    GO TO EXIT ;
LEVEN: FOR I := 1 STEP 1 UNTIL M DO
  BEGIN
    C[I] := RC[I] ;
    A[I,I] := WT2 × A[I,I]
  END ;
    WRITE (PRINT,CORR) ;
    GO TO JORDAN ;
EXIT: END.
```

CHAPTER III

CALORIMETER DESIGN, CONSTRUCTION, AND OPERATION

There are two fundamental calorimeter designs commonly used in studies of the thermodynamic properties of solids. These are the adiabatic calorimeter and the dropping calorimeter. The designs are more complementary than competitive; traditional versions of the adiabatic calorimeter perform well at low temperatures while the dropping calorimeter is usually selected for high-temperature work. There is no basis for preference of one design over another for all situations. The calorimeter to be built for this work was intended to be a general-purpose device for future research. The design, therefore, while restricted to one of the fundamental models, was required to have some of the capability of both. That is to say, the calorimeter built for this work was required to operate both above and below room temperature and to have sufficiently high absolute precision to permit the detection of small thermal effects.

The adiabatic calorimeter consists of a fixed sample holder fitted with a heater and a thermometer and surrounded by a shield which is maintained at precisely the same temperature as the sample to prevent heat leakage between the sample and the environment. A measurement is made indirectly by passing to the sample a measured amount of heat, usually in the form of electrical energy, and observing the rise in temperature. Because the temperature and electrical energy can be measured precisely,

and the starting temperature need not be far below the final temperature, small intervals in H(T,v) may be studied with precision. Such precision is valuable in studies of high-order transitions. There are many experimental variables to be controlled, however. For precise work, rather sophisticated control systems are needed; thus the system is usually expensive. It is, however, the generally preferred design for precise work at low temperatures where heat exchange by radiation is not a serious problem. The upper limit of the adiabatic calorimeter is usually taken to be 300 to 400°K.

The dropping calorimeter consists of two distinct units, usually mounted one above the other. The upper unit, called a "furnace" though it may not be a furnace in the usual sense, holds the sample and brings it to equilibrium with itself at some desired temperature. The sample holder is designed so that the thermometer is either inside the sample ampoule, intimately in contact with it, or in the same thermal environment. When the sample reaches equilibrium at the desired temperature, a release mechanism drops it into the lower unit, the receiver, which is at a different temperature. The release mechanism, typically, is a wire or thread which may be broken by remote control. The enthalpy change of the receiver when the sample is dropped into it is taken to be the enthalpy change of the sample between the equilibrium temperature of the "furnace" and the equilibrium temperature of the receiver and sample. Because the dropping calorimeter is usually used at high "furnace" temperatures with the receiver near the thermodynamic standard of 298.15°K, the enthalpy change is usually large and great absolute precision is needed to detect small changes in H(T,v).

There are two common types of receiver: the non-isothermal and the isothermal. The first is the more popular. It consists of a massive block of copper or some other good conductor of heat, which rapidly and evenly distributes the sample's heat throughout its mass. A vessel containing a stirred liquid is sometimes used for the same purpose. The block is fitted with a sensitive thermometer. The amount of heat released or absorbed by the sample is calculated from the temperature change of the block and the known $H(T,v)$ function. In practice, the block is made sufficiently massive to make the temperature change small, allowing calculations to be based on the assumption that the block's heat capacity is constant. Less common is the isothermal receiver. The region around the sample holder of the isothermal receiver contains a pure material, the working medium, at a first-order transition temperature with both phases present and in equilibrium. A solid-liquid transition near 298.25°K is usually used. When the sample is introduced into the receiver, some of the working medium melts or freezes without an accompanying change in temperature. The mass of the working medium melted or frozen may be determined from its volume change, using the densities of the two phases. The enthalpy change is determined from the mass of material melted or frozen and the heat of fusion of the material.

A dropping calorimeter with an isothermal receiver was selected for this work. The decision was based on the following considerations. The design requires very little sophisticated instrumentation; one precise control and two precise measurements are required. Control must be exercised on the leakage of heat between the receiver and the environment. The leakage must be reduced to a negligible amount because of the

great difficulty involved in correcting for it. The temperature of the sample must be measured precisely while it is in the "furnace." The volume change of the working medium must be measured precisely. At the time that the decision was made, a platinum resistance thermometer and an analytical balance were already available to perform these measurements; the problem of heat leakage was left to the detailed design. The ultimate precision of a calorimeter of this design is very great, probably 0.002 calorie with the measuring devices just mentioned. The ultimate precision cannot be attained, of course, and it has not been closely approached in any existing calorimeter of this design. In fact, this design is frequently exploited for its convenience only and the capability for high precision is ignored. In such designs, volume changes are read from a calibrated capillary. Although the use of a cathetometer could increase the precision greatly, it is better to measure the volume change by weighing material expelled from or drawn into the receiver. In practice, an enthalpy difference of 0.1 calorie can be detected easily; this level of precision is almost independent of the magnitude of the total enthalpy change being measured. It is this feature which allows the dropping calorimeter with an isothermal receiver to be considered favorably for detailed studies of $H(T,v)$. There are certain problems, however, which have prevented the widespread acceptance of this design. First, and most difficult, the working medium must be exceptionally pure. Water is most commonly used because it is easily freed of most of the harmful impurities by multiple distillation, but the problem of air removal remains. In addition, because the densities of solid and liquid water are so nearly

equal and because the heat of fusion is rather high, the use of water dictates an unnecessary loss of sensitivity. Most of the alternatives to water are organic compounds which are notoriously difficult to purify. Second, the solid phase of the working medium must be formed in a manner which does not introduce strains which would affect its heat of fusion. This problem is usually overcome by very slow freezing, sometimes requiring hours or days. Third, because of the low thermal conductivity of most substances suitable for use as a working medium, users of the isothermal receiver have found the approach to equilibrium after a drop to be so slow that the measurement is not completely determinate. In practice, this slow approach to equilibrium causes the drift curves before and after a drop to be non-parallel because of the slow transfer of heat to or from the solid phase of the working medium. The design of the calorimeter for this work has minimized or eliminated the problems associated with the isothermal receiver while maintaining the advantages.

Calorimeter Design and Construction

The calorimeter designed for this work deviates markedly from those used in other laboratories. To solve the problem of slow approach to equilibrium, no insulating materials were used in the construction of the receiver. The receiver is constructed of massive aluminum to assure rapid and even distribution of heat. Heat leakage is minimized by isolation, thermostatic control, and thermal damping. A large area is provided for building the mantle (the solid phase of the working medium) by a set of fins. It is not necessary to build a mantle thicker than 0.07 cm, compared to about one cm for other designs. The thin mantle, built slowly,

has been shown in this study to be essentially free of strain. Because heat must travel through only a thin layer of liquid to reach the mantle, the response is rapid. The "furnace" is made from a large single block of aluminum to provide thermal inertia. The sample-release mechanism provides metal-to-metal contact between the "furnace" and the sample ampoule over most of the ampoule's surface to assure rapid approach to equilibrium even at low temperatures. The use of high thermal inertia, good conductivity, and physical contact with the sample provide precision in temperature observation and control superior to the conventional design with the opposite characteristics. The conventional design relies on radiation and conduction through the furnace atmosphere to establish thermal equilibrium with the sample. For this reason, it may not be used below about 400°K. The efficacy of the "furnace" used in this work does not depend strongly on temperature. It may be used at temperatures below ambient.

The sample ampoule is made from Pt - 10% Rh alloy. The alloy is strong, abrasion resistant, oxidation resistant, has good thermal conductivity, and undergoes no known transitions below the melting point. It was selected as second choice. A copper or silver ampoule clad with a platinum-rhodium or platinum-iridium alloy would be better, but no bids for the fabrication of such an ampoule could be obtained. The ampoule is illustrated in Figure 2. The interior walls of the receiver and the release mechanism of the "furnace" match the conical shape of the ampoule so that the ampoule is snugly seated when it is sitting in the "furnace" and when it drops into place in the receiver. The vaned radiator is lo-

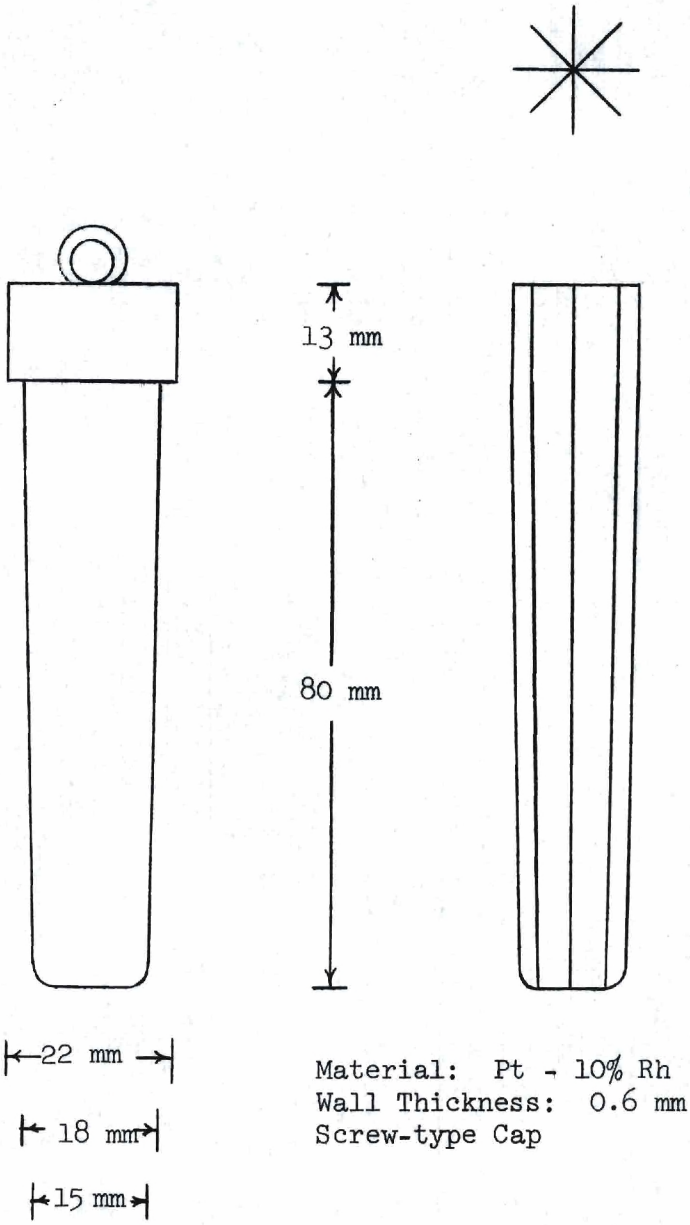

Figure 2. Calorimeter Ampoule Assembly

cated inside the ampoule to aid in transferring heat to and from the sample. The ring at the top is used only for recovery of the ampoule from the receiver.

A schematic diagram of the calorimeter assembly is shown in Figure 3.

The calorimeter is made almost entirely from aluminum alloy 6061-T6. The major portions of the "furnace" and the receiver are made from a single piece of six-inch diameter rod. The "furnace," sample release mechanism, and sample ampoule are shown in Figure 4. The ampoule, surrounded by three "leaves," sits inside the lower portion of the plunger at the right of the picture. The plunger sits inside the heat sink at the left. The thermometer well extends to the bottom of the upper portion of the plunger. When the "furnace" is assembled, it has very little void volume. When the plunger is lifted, the three "leaves" move outward from the central axis and allow the ampoule to drop. The heat sink is fitted with a set of electric heating bands which draws up to 20 amperes at up to 110 vAC. The output of the heater is controlled by an autotransformer fed by a constant-voltage transformer. There is a cylindrical aluminum container around the heat sink which is filled with vermiculite when the heater is used. In another mode of operation, the container is used as a constant-temperature bath, employing phase transitions of various materials to maintain a constant temperature. In this work, subliming CO_2, melting water, and boiling water were used in this way, but others could be used. The container is surrounded by eight inches of rigid polyurethane foam.

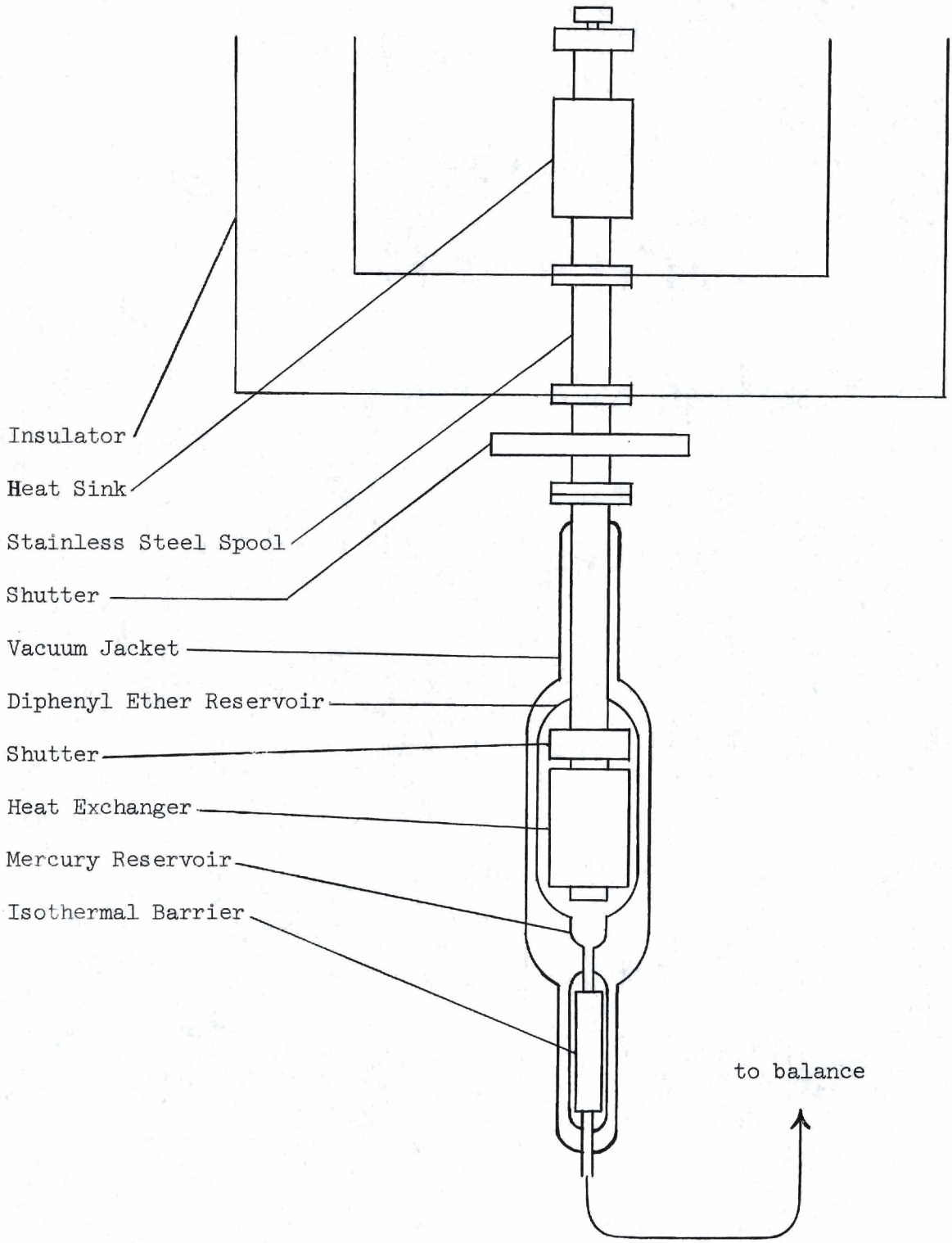

Figure 3. The Calorimeter Assembly

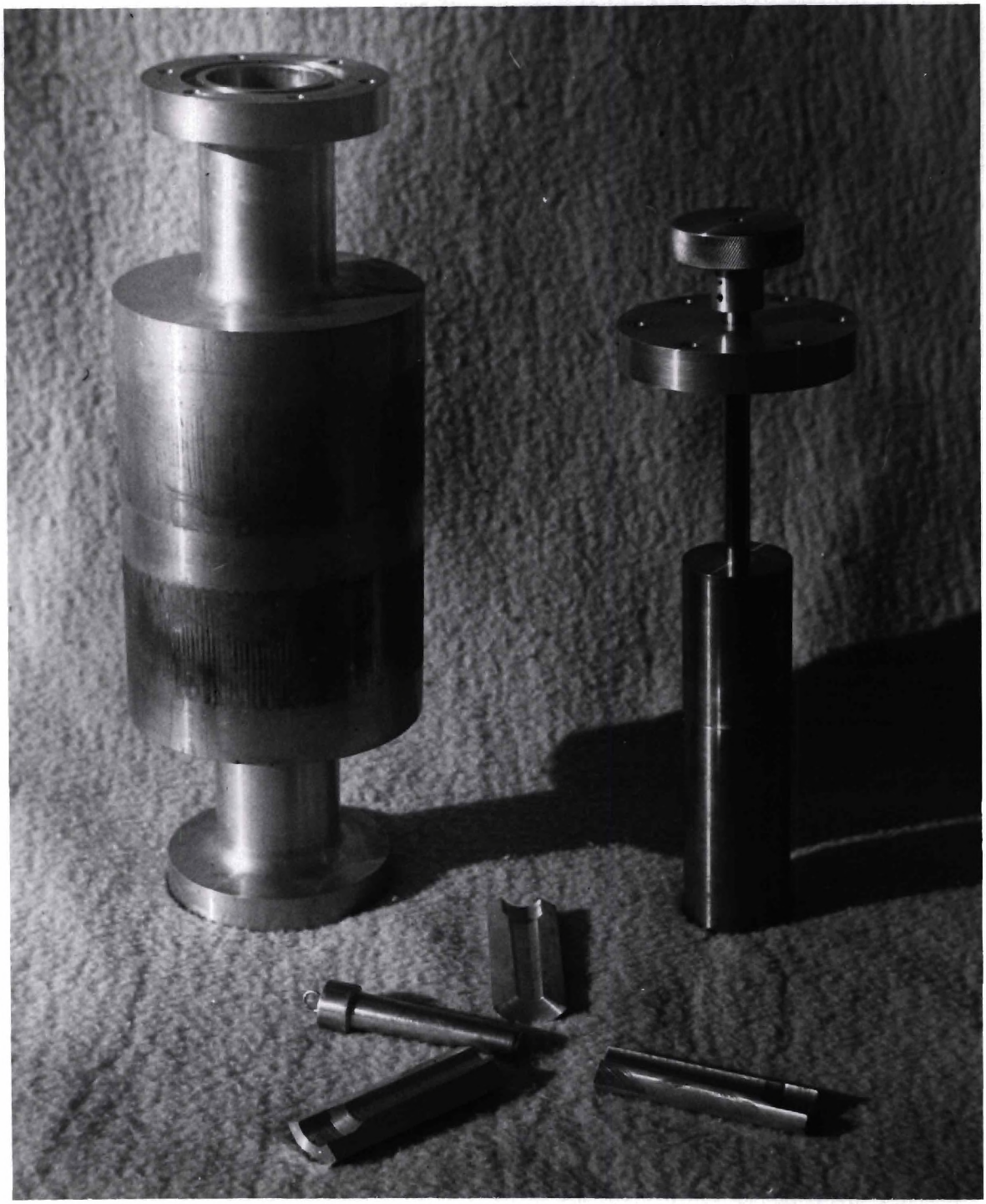

Figure 4. Calorimeter "Furnace," Sample Release Mechanism, and Sample Ampoule

Just below the heat sink is a thin-walled stainless steel spool which provides a path for the dropping ampoule but conducts little heat. At the lower end of the spool is an air-cooled radiator, held at the same temperature as the receiver, which blocks heat conduction between the "furnace" and the receiver. The radiator contains a solenoid-operated shutter which blocks the radiation of heat between the "furnace" and the receiver.

The receiver is attached below the radiator. The outer wall of the receiver is a vacuum jacket. The next wall is the working medium vessel. The innermost portion is the heat exchanger. The working medium vessel envelopes the heat exchanger rather closely, touching at six sharp points. The bottom of the working medium vessel is a mercury reservoir. The primary support for the working medium vessel and heat exchanger is a sample guide, a two-inch pipe segment 20 inches long, which is connected at the top to the vacuum jacket and to the radiator. The purpose of the great length of the sample guide is thermal damping to smooth out the periodic oscillation of the thermostat. The lower end of the working medium vessel is connected to a small lead-out tube for the mercury. The lead-out tube is short, but it is surrounded by an independent heat exchanger which prevents heat transfer by the tube. The filling tube runs through the vacuum jacket at the top, parallel to the sample guide.

The heat exchanger is shown in Figures 5, 6, and 7. Starting at the top, the bore of the upper portion is tapered to guide the sample through a manually operated shutter which prevents the loss of heat by a hot sample by radiation while it cools to the temperature of the receiver. The guide is intended only to prevent damage to the ampoule;

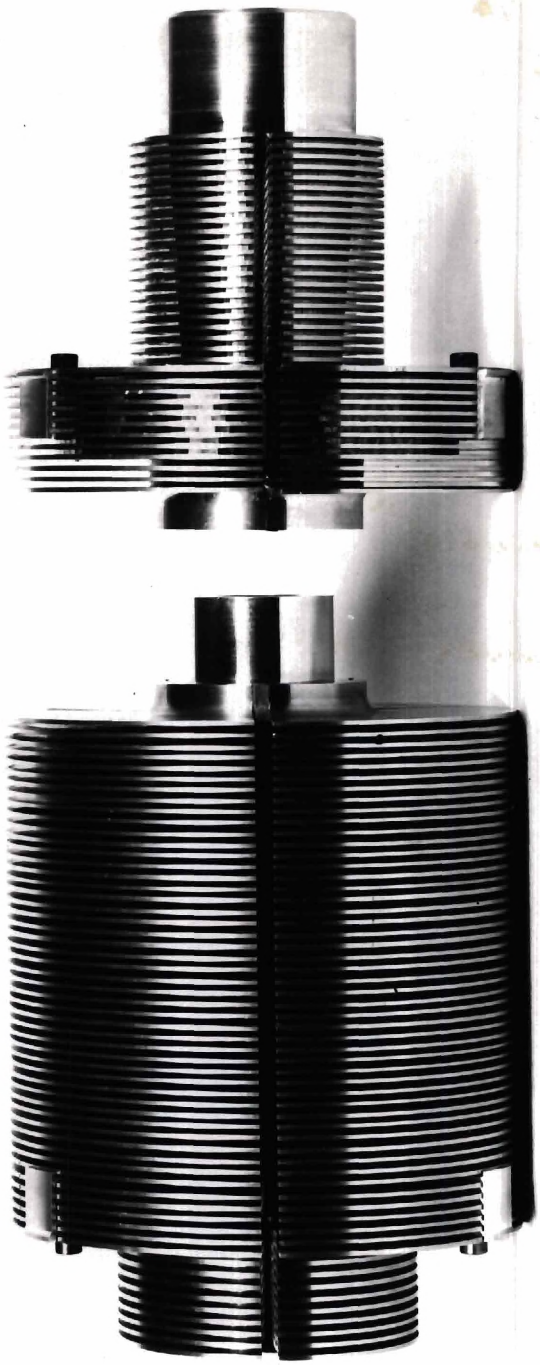

Figure 5. Upper and Lower Portions of Heat Exchanger before Assembly

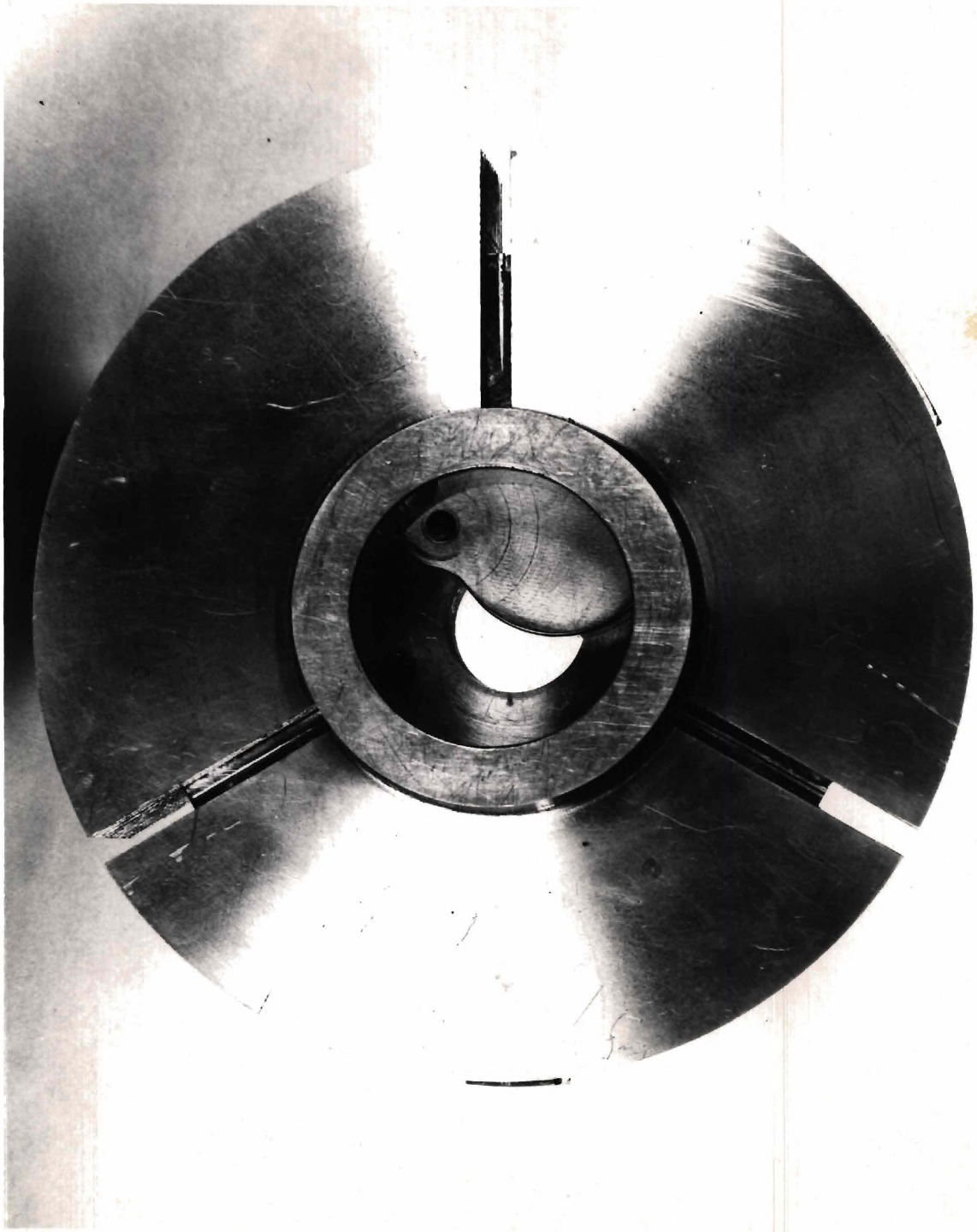

Figure 6. Detail of Radiation-absorbing Shutter in Heat Exchanger

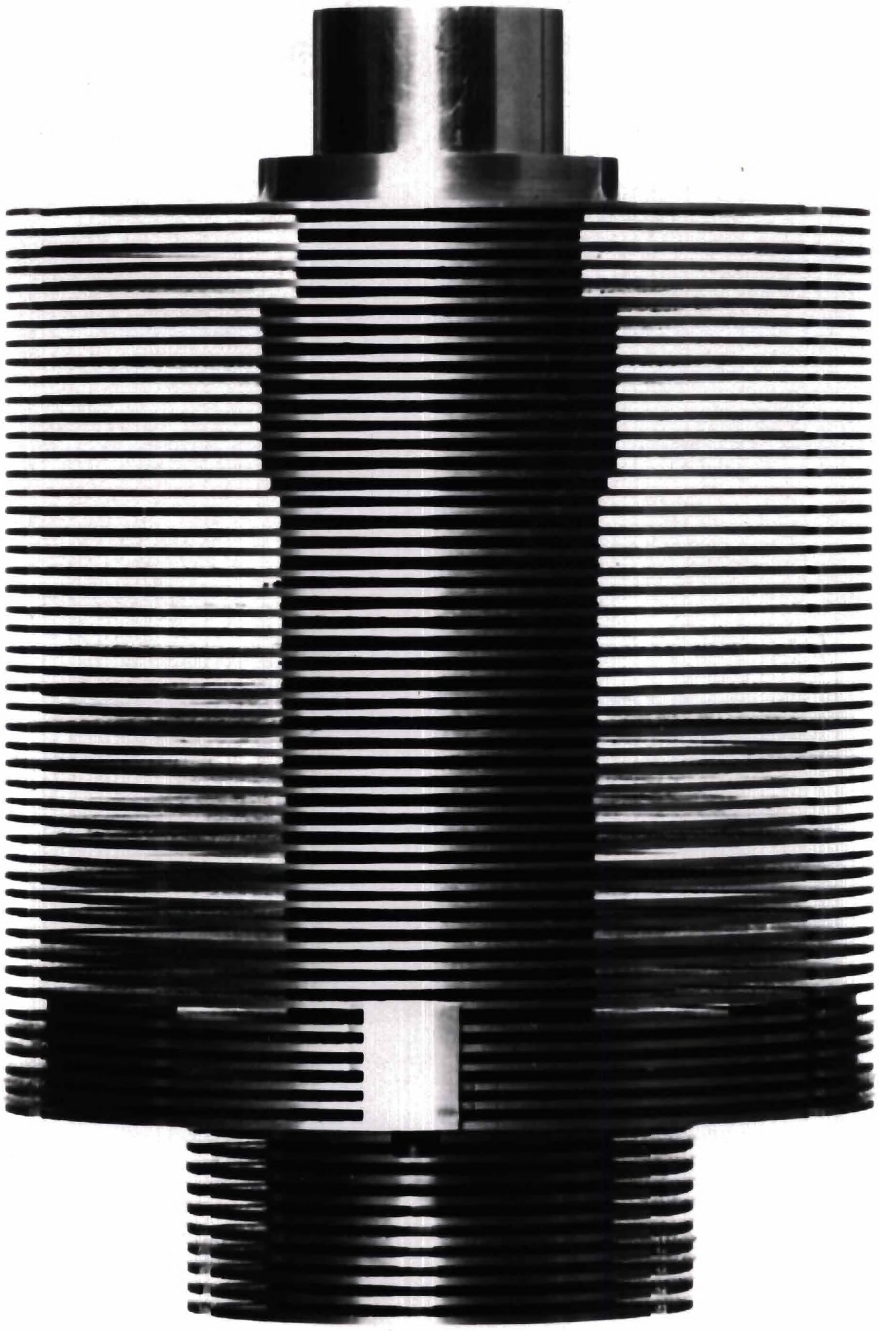

Figure 7. Lower Portion of Heat Exchanger

during a normal drop, the ampoule touches nothing until it reaches the lower portion of the heat exchanger. Starting at the top of the lower portion, the bore is a right circular cylinder, 0.020 inch larger than the cap of the sample ampoule. As the ampoule drops through this region, it is slowed by air (or other gas) in the receiver compressed by the ampoule.

The prominent feature of the heat exchanger is a set of fins, cut from a solid rod using a slitting saw. The fins are one-sixteenth inch thick and one-sixteenth inch apart. The depth of the cut used to form the fins varies so that the wall thickness of the heat exchanger may be nearly constant, but the average width is about two inches. The purpose of the fins is to conduct heat to or from the mantle, to support the mantle, and to provide a large area on which the mantle may be built. The large area allows a massive mantle to be built in thin sheets and provides a large number of nucleation sites to initiate freezing. In models developed at other laboratories, the prototypes of the fins have served primarily as supports for the mantle.

All joints in the receiver were made by inert-gas-shielded arc welding. They were tested for tightness by a helium leak detector. All compartments of the receiver were required to maintain 10^{-6} torr. The sub-assemblies ("furnace," spool, radiator, receiver) are joined by bolted flanges with Teflon "O"-rings.

The receiver and radiator are mounted inside a thermostatted air bath. A blower passes room air, already adjusted to a temperature slightly below the transition temperature of the working medium, through

a series of controlled electrical grid heaters and past a pair of sensitive thermistors which serve as sensors for the heater control. Short-term deviations were found to be less than 0.01°K with a period of eight seconds and long-term deviations were found to be 0.03°K. The long-term deviations were not significant for the period of a normal experiment. The control unit for the heaters, a thyratron type, was built for this application. It is not a commercial unit.

The volume change of the working medium is determined by mercury balance. The mercury reservoir is located inside the receiver to minimize problems of heat leakage and plugging of the lead-out tube by freezing. The latter proved to be a serious problem in attempts to use an external mercury reservoir or to dispense with mercury by direct weighing of the working medium. An analytical balance (Beckman model B-5), mounted beside the air bath, is used to weigh the mercury.

Temperature measurements were made with a platinum resistance thermometer (Leeds and Northrup Co., Catalog No. 8163-C, Serial No. 1547845) using a Müller bridge (Leeds and Northrup Co., Catalog No. 8069-B, Serial No. 1551895). A galvanometer (Leeds and Northrup Co., Catalog No. 2284-B) was used as a null indicator.

The Working Medium

The working medium selected for this work is diphenyl ether. Diphenyl ether offers several advantages over the alternative working media. These were first recognized by Sachse[33] in 1929. Among the advantages are:

1. Diphenyl ether melts at 300.03°K. This temperature is conveniently close to the thermodynamic standard temperature of 298.15°K; this

closeness permits easy and accurate interpolation or extrapolation of calorimetric measurements to standard values. The melting point is also conveniently close to the normal room temperature. This closeness simplifies the problem of minimizing heat exchange with the environment.

2. The nominal value of the calorimeter constant of a receiver which employs diphenyl ether is low because of the rather low heat of fusion (24.2 calories per gram) and the rather high volume change on freezing or melting (0.094 cm^3/gram). The low calorimeter constant permits high sensitivity, about three times that of the ice calorimeter.

3. The chemical properties are desirable in several respects. Diphenyl ether is stable under most conditions. In spite of its high boiling point (532°K), diphenyl ether can be distilled in air at atmospheric pressure without decomposition. It is inert to basic aqueous solutions which are used to remove a large fraction of a primary impurity, phenol. Its toxicity is very low.

The major disadvantages to the use of diphenyl ether, which are not peculiar to it, are that it is a poor conductor of heat and it is difficult to obtain in a state of purity sufficient for precise and reproducible calorimetric measurements.

Diphenyl Ether Purification

The primary impurities which must be removed from the diphenyl ether are phenol, water, and air. Four steps were used to remove the impurities: solvent extraction, fractional distillation, zone refining, and degassing.

Solvent Extraction. Practical-grade phenyl ether from Distillation Products Industries of the Eastman Kodak Corporation was extracted with

concentrated aqueous potassium hydroxide solution to remove acidic impurities, notably phenol, and stored over solid KOH pellets for at least one week. The storage time varied according to the demands of the later stages of purification.

Fractional Distillation. It was necessary to build a still for fractional distillation of the diphenyl ether. The still was a simple, packed-column type. It employed a five-liter glass pot heated by a Glas-Col heating mantle. The pot was joined to the reflux column by a standard ball-and-socket joint. The reflux column was made from 18 mm glass tubing, packed with three-sixteenths inch glass helices, and surrounded by an electrically-heated glass adiabatic shield. The column was equivalent to about 50 plates. Surmounting the column was a stream splitter, which operated on the condensate stream to control the reflux ratio.

Because of the large amount of product required, it was necessary to distil several batches. For each batch, the pot was initially charged with 3.5 liters of diphenyl ether from the solvent-extraction step. After boiling began, distillation was allowed to proceed for a few minutes with the stream splitter open to remove most of the low-boiling impurities. Then, under total reflux, the diphenyl ether was boiled for a minimum of 24 hours to pyrolyze some of the remaining impurities. Periodically during this period, the stream splitter was opened for a few minutes to remove the low-boiling pyrolysis products. At the end of this period, the material in the pot was a rather dark brown. The reflux ratio was then set to about 10 and the distillation was allowed to proceed until about three liters of product was collected. The rate was about one liter per

day. When the distillation of a batch was complete, the pot was cleaned and the process was repeated. Approximately 12 liters of distilled diphenyl ether was collected.

Zone Refining. The design and construction of a zone refiner suitable for the purification of diphenyl ether proved to be somewhat troublesome. Some of the problems which were encountered are mentioned here so that they may be avoided in the future. The major difficulty is the large volume change on melting, one of the features which makes diphenyl ether desirable as a working medium. Three entirely different zone refiners were constructed and tested; only the third proved to be entirely satisfactory.

The first model was air cooled and employed a single tube, 32 mm in diameter, with an active length of four feet. The heater was a loop of nichrome wire, which was screw driven by a geared-down electric motor and manually returned by reversing the screw. Operated vertically, with upward heater travel, the refiner invariably suffered a broken tube. When the refiner was operated vertically with downward heater travel, it was difficult to refreeze the diphenyl ether because of convection currents in the air above the heater and in the liquid above the heated zone. Shielding the heater had little effect. The performance was improved by horizontal operation with a partially filled tube, but the zone length was impractically large, even when the refiner was operated in a refrigerated room at 277°K. A lower temperature might have been effective.

The second model consisted of a helix of 11 mm diameter glass tubing with a diameter of 11.5 inches and a length of 24 inches. The helix

was filled with diphenyl ether, mounted on a slowly rotating mandrel, and almost totally immersed in an ice bath. A set of nichrome heating wires was mounted just above the exposed surface of the helix. No way was found to relieve the pressure due to melting and the tubes invariably broke. If a flexible tube which does not contaminate the diphenyl ether could be found, this method could be made to work. This method is highly desirable because of the large number of zones which move down the helix and the large effective-length to zone-length ratio.

The final model proved to be satisfactory. Cooling for the system was provided by a bath of refrigerated water maintained at 294°K. Four glass tubes, 32 mm in diameter, with an effective length of nine feet, were mounted on a frame immersed in the bath. A grid of nichrome heating wires, sealed against the bath in an aluminum box with natural-rubber seals, surrounded the tubes. The box traveled on rails mounted on the frame. The drive mechanism was so designed that forward travel of the heaters was accomplished by worm-gear action at a slow rate and reverse travel was accomplished by rack-and-pinion action at a high rate. The same gear set was used for both. The design of the tubes provided for automatic initiation of freezing and easy withdrawal of impure material. The capacity was about four liters with the tubes half full.

One liter of distilled diphenyl ether was placed in each tube. Using a vacuum pump with a liquid-nitrogen trap, the pressure in the tubes was reduced to a value just above the vapor pressure of diphenyl ether at the bath temperature and the liquid was allowed to freeze. While the pumping was continued, the zone was passed once down the tubes.

The tubes were then filled with dry helium, which is only slightly soluble in diphenyl ether, at slightly greater than atmospheric pressure. Refining was then begun; the rate of zone travel was set at 0.21 foot per hour and the zone length at three inches. After each fourth pass, about 0.020 liter of material was removed from the "impure" end of each tube. The refining process was terminated after 17 passes. When the zone refining was complete, each tube contained a clear, apparently single crystal which occupied about half the length of the tube, starting about three inches from the "pure" end. The tube was cut at the boundaries of the crystal. The purified diphenyl ether was removed by heating the tube section in a stream of warm air and stored for later use. The refining operation was carried out three times; about five liters of zone-refined diphenyl ether was collected. Detailed cryoscopic determinations of the purity of the product were not made. However, Dr. John R. Dyer of the School of Chemistry analyzed a sample of the material, using a gas chromatograph. Under conditions which would have detected 0.05 to 0.1 percent of impurities, no impurities were found. It is felt that the impurity concentrations were far below the detection limit of the gas chromatograph.

Degassing and Filling. A filling tube was built to degas the purified diphenyl ether and to fill the receiver of the calorimeter. The filling tube consisted of a five-liter bulb sealed to a straight tube, 75 mm in diameter and 24 inches long, which was constricted at the end to accommodate a Swagelok fitting on the receiver. Diphenyl ether was placed in the bulb and partially degassed by repeatedly freezing and

thawing the material under vacuum. The diphenyl ether was then frozen and the filling tube was connected to the receiver of the calorimeter. The entire system was evacuated. To remove the remaining gas from the diphenyl ether, the solid was melted slowly and allowed to run down the tube toward the receiver. As the diphenyl ether ran down the tube, it was again frozen and melted several times before it reached the receiver. The filling operation required 210 hours of almost continuous activity; this is an area in which efforts should be made to automate the process. When the receiver was full, as indicated by the liquid levels in the filling and delivery tubes, the filling tube was pressurized momentarily with dry helium to force liquid out of the delivery tube. A reservoir of boiled distilled mercury was placed under the delivery tube and the filling tube was again evacuated to draw mercury into the receiver. The filling valve on the receiver was then closed and the receiver was ready for use.

Experimental Measurements

The sequence of operations necessary to perform a measurement with the calorimeter is as follows.

1. Build a mantle. To do this, immerse the mercury delivery tube in a mercury reservoir on the balance pan. Drop small pieces of dry ice (two grams or smaller), one at a time, into the receiver and note the mercury displacement produced by each one. Before dropping each piece of dry ice, wait until the mercury displacement rate is nearly zero. Add weighed portions of mercury to the reservoir as necessary. Discontinue when the mantle size, as indicated by its history and the

mercury displacement, is about 50 percent greater than is needed for the next measurement. Building a mantle routinely takes about two hours.

2. While the mantle is being built, bring the "furnace" to a temperature near the desired value. This may be done in either of two ways, depending on the type of control exercised on the "furnace." If a first-order phase transition is used to control the temperature, load the material which undergoes the transition into the container which surrounds the heat sink. If the transition temperature is below ambient, allow the "furnace" to approach the equilibrium temperature; if the transition temperature is above ambient, raise the temperature to the transition point and maintain it at this level with the heater. If this method of control is used, temperature control is automatic. If the phase transition is not used, heat the sink to a temperature about 1.0°K above the desired temperature and establish a cooling rate of about 0.05°K per minute.

3. Record the weight of the mercury reservoir as a function of time. The air bath temperature is set initially to establish a drift rate of approximately 0.0010 gram per minute. A positive drift rate has been recommended by other users of the isothermal receiver, but the direction of the drift does not appear to be important with this receiver. However, a positive drift was used in all experiments reported in this work. When making a weighing to determine the mercury displacement, dip the end of the delivery tube into the reservoir before making each reading. Record the time when the tube is dipped and complete the weighing before the next drop of mercury is delivered.

4. When the "furnace" is within 0.01°K of the desired temperature, note this temperature, open both shutters, drop the sample, close the shutter in the heat exchanger, close the shutter in the radiator, and measure the "furnace" temperature again. These operations must be performed as quickly as possible. With practice, the entire sequence takes about 30 seconds. The shutters are open from two to five seconds. If the two temperature readings differ by more than 0.03°K, start over at step 2.

5. Continue to record the weight of the mercury reservoir as a function of time until it varies at a constant rate. The rate reaches a constant value after about five minutes. The final rate should be equal to the initial rate. It was found to be so in all cases.

The drop temperature is determined by linear interpolation, using the recorded temperatures, the recording times, and the drop time. The mercury displacement is determined by the separation of the two drift lines. If the initial and final drift rates are not equal, it is recommended that the data be discarded rather than corrected. In the experiments performed, unequal drift rates were not observed.

Base Line Determination

The enthalpy change of the sample ampoule is included in every measurement. To determine the enthalpy change of a sample, the mercury displacement due to the ampoule must be subtracted from the total displacement. Because the composition of the ampoule is not known precisely and because few precise enthalpy data for the ampoule material, Pt - 10% Rh, are found in the literature, it was necessary to determine H(T,v)

for the ampoule experimentally. It is neither necessary nor useful to convert the experimental values to standard energy units. They are reported as mercury displacement due to the empty ampoule as a function of temperature. The results are shown in Table 1.

Table 1. Ampoule Base Line

Temperature (°K)	Hg Displacement (grams)
194.61	-34.4818
273.15	- 8.5579
298.15	- 0.6002
351.08	16.3815
372.71	23.3609
380.03	25.7279
389.99	28.9745
400.09	32.2611
409.98	35.4895
420.10	38.7904
425.03	40.3947
429.92	42.0002
435.01	43.6726
440.11	45.3478
444.95	46.9420
450.40	48.7353

Weight of Pt - 10% Rh Ampoule:
164.8558 grams

Except for the temperatures 194.61°K, 273.15°K, and 372.71°K, the base line measurements were made before any others. Efforts were made to space the points about equally and to select temperatures from the resulting set for subsequent measurements. Such a procedure would sim-

plify the calculations considerably and reinforce the confidence in the results somewhat because of the directness of the method. It was not possible to do this exactly. It proved to be difficult to reproduce temperatures in the "furnace" to better than 0.02°K (although measurements could be made to 0.001°K), and it was necessary to make several measurements at temperatures between those used in the base line measurements. For these reasons, it was necessary to prepare a more extensive table, using all drop temperatures, by interpolation. To do this, the base line data above 372.71°K were divided into N-5 groups of consecutive points, where N is the number of points. A third-degree polynomial was fitted by a least-squares method to the first set of six points. The polynomial was used to calculate base line displacement values for all drop temperatures used which were less than that of the fourth point of the set. Third-degree polynomials were fitted to successive sets and used to interpolate between the third and fourth point of each set. In the last set, the polynomial was used to interpolate through the sixth point. The resulting values are tabulated in Tables 2 and 3.

Calorimeter Constant Determination

The calorimeter constant of an isothermal receiver is the heat equivalent to a unit mass of material displaced by the expansion or contraction of the working medium. In this case, it is the amount of heat in calories required to displace one gram of mercury by the melting or freezing of diphenyl ether. The calorimeter constant is defined as

$$K = \Delta H_f/(v_s - v_\ell)d_m$$

Table 2. Calorimeter Constant Determination

Temperature (°K)	Hg Displacement (grams)	Hg Displacement Due to Ampoule (grams)	$H_T - H_{300.03}$ (calories per mole from references 19 and 34	Calorimeter Constant (calories per gram of Hg)
194.61	-44.5413	-34.4818	-1652.7	19.003
273.15	-11.5419	- 8.5579	- 490.3	19.005
380.09	35.9100	25.7606	1667.4	19.002
430.12	59.2491	42.0650	2823.7	19.006
439.98	63.9404	45.3149	3060.2	19.004
			Average	19.004

Weight of Al_2O_3 : 11.7909 grams

Weight of Pt - 10% Rh Ampoule: 164.8558 grams

Table 3. Enthalpy ($H_T - H_{300.03}$) and Heat Capacity (C_p) of Sodium Nitrite

Temperature (°K)	Hg Displacement (grams)	Hg Displacement Due to Ampoule (grams)	$H_T - H_{300.03}$ (calories per mole)	C_p (calories per mole °K)
194.61	- 78.4946	-34.4818	-1615.8	
273.15	- 20.3796	- 8.5579	- 434.0	
298.15	- 1.4479	- 0.6002	- 31.1	
351.08	40.7148	16.3815	893.3	
372.71	59.1697	23.3609	1314.6	
380.12	65.9479	25.7606	1475.3	
390.08	75.2516	29.0071	1697.7	
400.21	84.8338	32.2938	1928.8	
409.99	94.5114	35.4896	2166.8	24.9
420.02	105.0971	38.7574	2435.4	28.9
430.11	116.8977	42.0640	2747.2	34.2
434.98	123.5069	43.6727	2930.8	43.1
435.50	124.2679	43.8369	2952.7	45.8
436.03	125.0813	44.0010	2976.5	51.5
436.19	125.4343	44.0667	2987.1	56.8
436.30	125.6218	44.0995	2992.8	70.9
436.40	125.8356	44.1323	2999.4	109.0
436.48	126.1484	44.1651	3009.7	179.6
436.59	126.6391	44.1980	3026.5	267.0
436.71	127.3691	44.2308	3052.1	241.7
436.80	128.1838	44.2636	3080.8	161.3
436.91	128.6766	44.2965	3097.7	107.1
436.99	129.0131	44.3293	3108.8	54.8

Table 3. Enthalpy ($H_T - H_{300.03}$) and Heat Capacity (C_p) of Sodium Nitrite (Concluded)

Temperature (°K)	Hg Displacement (grams)	Hg Displacement Due to Ampoule (grams)	$H_T - H_{300.03}$ (calories per mole)	C_p (calories per mole °K)
437.11	129.2432	44.3621	3116.1	45.3
437.21	129.4124	44.3950	3121.1	43.9
437.29	129.5651	44.4278	3125.5	42.8
437.40	129.7154	44.4607	3129.8	47.8
437.49	129.8718	44.4935	3134.3	48.2
437.60	130.0357	44.5263	3139.1	49.2
437.71	130.2017	44.5592	3144.0	49.1
437.79	130.3682	44.5920	3148.9	46.0
437.89	130.5305	44.6249	3153.7	45.1
438.00	130.6864	44.6577	3158.2	41.5
438.08	130.8355	44.6905	3162.5	39.8
438.19	130.9773	44.7234	3166.5	
438.40	131.2472	44.7891	3174.0	
438.58	131.5008	44.8548	3180.9	
439.01	131.9821	44.9862	3193.7	
439.49	132.5630	45.1504	3209.0	
439.99	133.1272	45.3152	3223.7	
450.31	143.6332	48.7027	3485.0	

Weight of $NaNO_2$: 35.7241 grams

Weight of Pt - 10% Rh Ampoule: 164.8558 grams

Calorimeter Constant : 19.004 calories per gram of Hg

where ΔH_f is the heat of fusion of the working medium, v_s and v_ℓ are the specific volumes of the two phases of the working medium at the transition temperature, and d_m is the density of the displaced material which is weighed. Although all of the quantities which appear on the right-hand side of the equation are subject to precise measurement by conventional means, the literature values are not useful because v_s and v_ℓ are so nearly equal. The calorimeter constant is easily measured by observing the response of the calorimeter to a known heat effect. With proper instrumentation, the calibration could be done electrically. As an alternative, requiring little instrumentation, a well-established first-order phase transition, such as the vaporization of water, could be used. For this work, a less fundamental but equally accurate method was selected: the response of the calorimeter to drops of a material whose $H(T,v)$ function is well established. Aluminum oxide was selected for this purpose. The International Calorimetry Conference and the National Bureau of Standards have selected aluminum oxide as a standard for enthalpy and heat capacity measurements. The results of careful measurements by the National Bureau of Standards[19, 34] are in the literature. These values are used in this work.

The aluminum oxide used is a standard sample of synthetic sapphire obtained from Dr. W. T. Ziegler of the School of Chemical Engineering at the Georgia Institute of Technology. The sample was obtained by Dr. Ziegler from Dr. Wichers of the Chemistry Division of the National Bureau of Standards. The sample was prepared for the measurements by washing with water, washing with acetone, drying overnight at 463°K in the open sample ampoule, and sealing the ampoule while the sample was still

hot.

The measurements necessary for the calculation of the calorimeter constant are reported in Table 2. The average value for five measurements is 19.004 calories per gram of mercury. The standard deviation is 0.0016 calories per gram. A calorimeter constant determined in this way is not defined exactly by the equation just given; it reflects certain characteristics of the calorimeter, such as the dropping energy of the sample. Such effects are small, however, and a comparison of the calorimeter constant with those of similar calorimeters is interesting. The constant for this calorimeter is in good agreement with the value of 19.01 reported by Giguère, et al.[35] It is in fair agreement with the value of 18.95 reported by Hultgren, et al.,[36] who used a capillary to measure the volume of mercury displaced. Agreement with Holmberg's value of 0.0488 gram per calorie (20.5 calories per gram)[37] is not good. Although 20.5 calories per gram of mercury is the accepted interpretation of the constant for Holmberg's calorimeter, the value which he reported is 0.0488 gram per degree, or scale division. The scale was not defined.

An independent estimate of the standard deviation of the calorimeter constant can be made if the calorimeter constant is considered to be a linear combination of random variables.[38] Examination of the National Bureau of Standards' data for the enthalpy of aluminum oxide shows that 95 percent of the data lie within 0.03 percent of a smoothed curve which represents all of the data. This deviation is approximately equivalent to a standard deviation of 0.015 percent. The standard deviation for mercury-displacement determination is estimated to be 0.0002 gram for measurements which employ the filled sample ampoule and 0.0004 gram

for measurements which employ the empty ampoule. The larger value for the empty ampoule is adopted because the value of the displacement must be found by interpolation. Using these values, the standard deviation of the calorimeter constant is estimated to be 0.0029 calorie per gram of mercury, in acceptable agreement with the measured value. Because the measured value represents a small sample, the estimated value is probably the more realistic. Incidentally, these calculations show that mercury displacements need be recorded to the nearest milligram only if the National Bureau of Standards' data are used for calibration.

The Thermodynamic Properties of Sodium Nitrite

The thermodynamic behavior of sodium nitrite has been known to be anomalous since the lambda transition near 436°K was discovered by Jaffray[39] in 1947. The existence of the anomaly near 436°K was confirmed by Ray[40] and by Nomura.[41] Hoshino,[42] Maruyama, et al.,[43] and Sakiyama, et al.[44] have reported that there are two anomalies near 436°K. In addition to the large lambda transition which peaks near 436°K, they report a very small peak in the heat capacity at a slightly higher temperature. Other anomalies have been reported at 373°K,[45] 451°K,[46] and 483°K.[47]

This study covers the temperature region from 194.61°K to 450.31°K, which includes five possible anomalies. The region near 483°K was not studied. The region near 436°K, however, was studied in detail.

Sodium nitrite for the work was supplied by Jean M. Ray, who prepared it from reagent-grade sodium nitrite by nine stages of fractional crystallization. The salt supplied by Mrs. Ray was prepared for this work by drying overnight at 463°K in the open ampoule and sealing while the sample was still hot.

The experimental results are shown in Table 3. The enthalpy data are based on a calorimeter constant of 19.004 calories per gram of mercury. The estimated maximum standard deviation, assuming the measured enthalpy difference to be a linear combination of random variables, is 0.06 calorie per mole. The heat capacity values are derived from the enthalpy data by numerical differentiation. Values are given in thermochemical calories (4.1840 joules/calorie).

Two peaks near 463°K are shown clearly by the heat capacity data, which are shown graphically in Figure 8. There is no evidence to support the observation of Sakiyama, et al.[44] that the lower transition becomes first-order near 436.6°K. It appears to be only a very steep lambda transition. The heat capacity values agree well with those of Sakiyama, et al.[44] except in the immediate vicinity of the peak near 436.6°K. Comparison with other studies is not possible because the data were not published. A third peak in this region, suggested by the thermal expansion studies of Maruyama, et al.,[43] was not observed. This work neither confirms nor disputes anomalous behavior near 373°K and 451°K. Neither appears in the results of this work, but the observations were widely spaced near 373°K and stopped just short of 451°K. If there is a transition in either region, it is too small energetically to be detected without more detailed study.

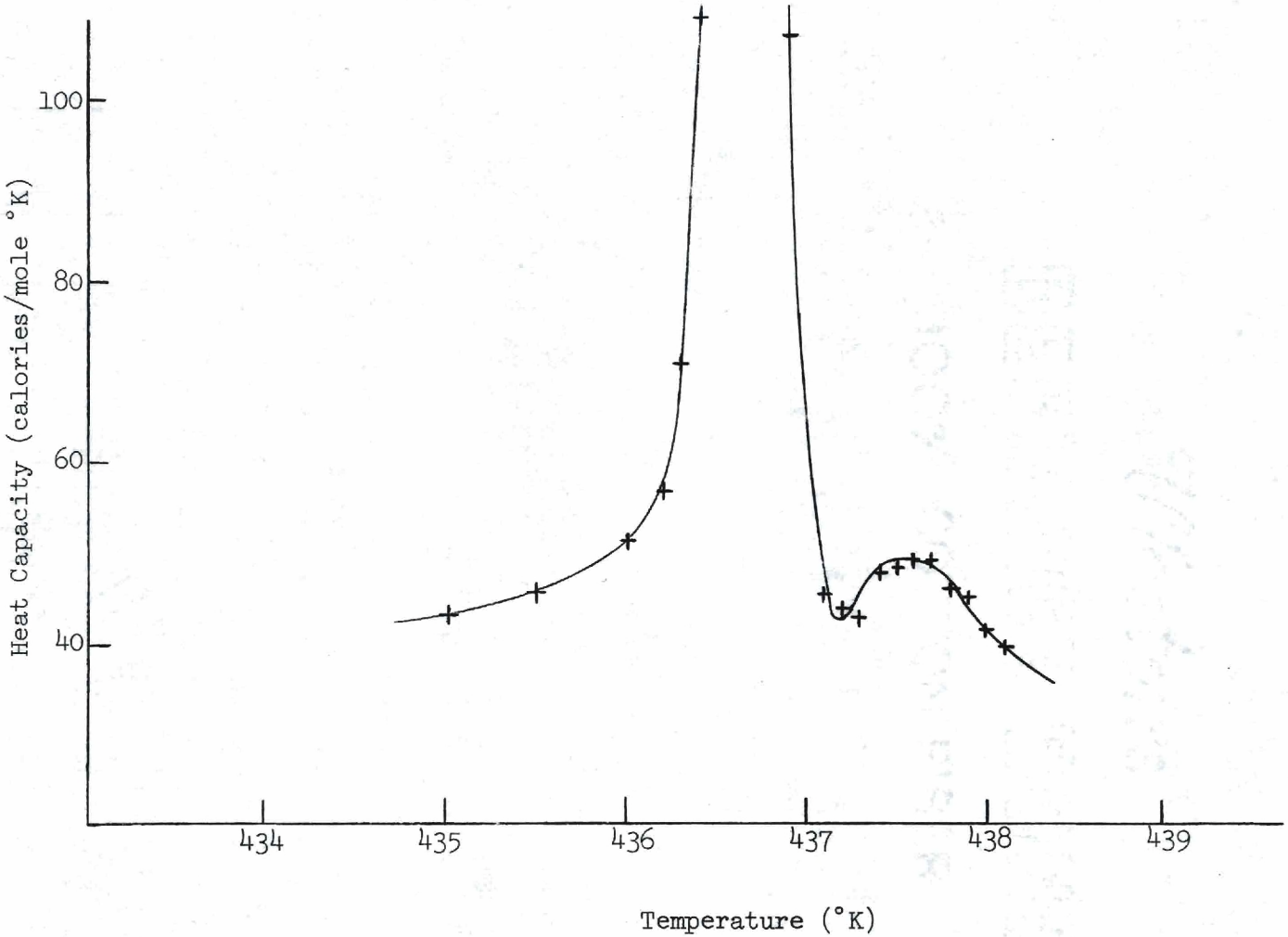

Figure 8. Heat Capacity of Sodium Nitrite in an Anomalous Region

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The Born approximation is superior to the more commonly used polynomial for the expression of calorimetric data. It has the advantage of greater precision over a much wider temperature range with fewer adjustable parameters. Because it is based on a realistic model of the vibrational behavior of solids, it can be used with comparative safety for the extrapolation of calorimetric data from about 50°K to 0°K. Expressions for most thermodynamic functions are obtained easily from the enthalpy expression by the use of tables. The use of the Born approximation for thermochemical calculations and for the concise reporting of calorimetric results as an adjunct to definitive data is recommended.

A new set of mathematical expressions for thermodynamic functions has been developed in this study. They are comparable to the Born approximation in their ability to express calorimetric data. The expression for the vibrational frequency distribution function on which they are based is capable of a more realistic approximation to the true frequency distribution than are those which precede it. The use of the new expressions for thermochemical calculations is not particularly attractive because the fitting procedures are difficult. Their use for studying vibrational frequency distribution is promising and is limited now only by the precision of calorimetric data and the speed of existing

computers. The Univac U-1108, recently installed on the Georgia Tech campus, represents a significant improvement in speed over the Burroughs B-5500 used in this work. The U-1108 might be used for studies of some simple crystals.

The calorimeter system designed and constructed in this study has proved to be precise, reliable, and reasonably simple to operate. It was demonstrated over a temperature interval of 195°K to 450°K. The estimated standard deviation for the set of measurements was 0.06 calorie, about what is expected of precise calorimetric equipment. The precision can be improved by mounting the entire calorimeter system on a stable base, preferably in the basement of a building, improving the temperature control of the laboratory, and substituting a bath of melting diphenyl ether for the air bath.

The solid selected for study was sodium nitrite, which is continuing to be the subject of active study by Japanese workers. There are few data in the literature for comparison, but the agreement with existing ones is good. Two anomalous peaks were found: one at 436.65°K and one much smaller one at 437.65°K. Several others which have been reported in the literature were not found.

APPENDIX

BERNOULLI NUMBERS AND DEBYE COEFFICIENTS

	Bernoulli Numbers	Debye Coefficients
1	$1.6666666666666666666666666667 \times 10^{-1}$	$-5.0000000000000000000000000 \times 10^{-2}$
2	$3.3333333333333333333333333333 \times 10^{-2}$	$1.7857142857142857142857142857 \times 10^{-3}$
3	$2.3809523809523809523809523809 \times 10^{-2}$	$-5.5114638447971781305114638384 \times 10^{-5}$
4	$3.3333333333333333333333333333 \times 10^{-2}$	$1.5782828282828282828282828283 \times 10^{-6}$
5	$7.5757575757575757575757575758 \times 10^{-2}$	$-4.3359418359418359418359418359418 \times 10^{-8}$
6	$2.5311355311355311355311355313 \times 10^{-1}$	$1.1625218305112485006664900 \times 10^{-9}$
7	$1.1666666666666666666666666667$	$-3.0701113217453086734132485 \times 10^{-11}$
8	$7.0921568627450980392156862745$	$8.0281901755008541582820417 \times 10^{-13}$
9	$5.4971177944862155388471177935 \times 10$	$-2.0851864993817622512901484 \times 10^{-14}$
10	$5.2912424242424242424242424242 \times 10^{2}$	$5.3898919920786750766681059 \times 10^{-16}$
11	$6.1921231884057971014492753623 \times 10^{3}$	$-1.3882687127467778378310684 \times 10^{-17}$
12	$8.6580253113553113553113553114 \times 10^{4}$	$3.5661409752632004092919642 \times 10^{-19}$
13	$1.4255171666666666666666666667 \times 10^{6}$	$-9.1414837231796572543790430 \times 10^{-21}$
14	$2.7298231067816091954022988506 \times 10^{7}$	$2.3394674567420686931697145 \times 10^{-22}$
15	$6.0158087390064236838430386853 \times 10^{8}$	$-5.9791473743448007953652337 \times 10^{-24}$
16	$1.5116315767092156862745098039 \times 10^{10}$	$1.5264729491574709354558315 \times 10^{-25}$
17	$4.2961464306116666666666666667 \times 10^{11}$	$-3.8935695969154493320205465 \times 10^{-27}$
18	$1.3711655205088332772159087948 \times 10^{13}$	$9.9238325325604504797201836 \times 10^{-29}$
19	$4.8833231897359316666666666667 \times 10^{14}$	$-2.5277500061891462404771064 \times 10^{-30}$
20	$1.9296579341940068148632668113 \times 10^{16}$	$6.4350609915575279614762167 \times 10^{-32}$
21	$8.4169304757368261500055371049 \times 10^{17}$	$-1.6374502817451167099403761 \times 10^{-33}$
22	$4.0338071854059455413076811594 \times 10^{19}$	$4.1649293637533924204403169 \times 10^{-35}$
23	$2.1150748638081991605601453877 \times 10^{21}$	$-1.0589945855843171660223982 \times 10^{-36}$
24	$1.2086626522296525934602731225 \times 10^{23}$	$2.6918152612611439921034012 \times 10^{-38}$
25	$7.5008667460769643668557200845 \times 10^{24}$	$-6.8403455754245302017856762 \times 10^{-40}$
26	$5.0387781014810689141378930370 \times 10^{26}$	$1.7378231663610432455486542 \times 10^{-41}$
27	$3.6528776484818123335110430827 \times 10^{28}$	$-4.4140715945588445145688068 \times 10^{-43}$
28	$2.8498769302450882226269146411 \times 10^{30}$	$1.1209578952230075166228000 \times 10^{-44}$
29	$2.3865427499683627644645981888 \times 10^{32}$	$-2.8461901168891707037522165 \times 10^{-46}$
30	$2.1399949257225333665810744800 \times 10^{34}$	$7.2255450160128777735983021 \times 10^{-48}$

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*The abbreviations used herein conform to the recommendations of Chemical Abstracts.

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